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Updated Process Flowsheets for Manganese Nodule Processing

By Benjamin W. Haynes, Stephen L. Law, and Riki Maeda

UNITED STATES DEPARTMENT OF THE INTERIOR

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UNITED STATES DEPARTMENT OF THE INTERIOR
James G. Watt, Secretary

BUREAU OF MINES
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As the Nation's principal conservation agency, the Department of the Interior has responsibility for most of our nationally owned public lands and natural resources. This includes fostering the wisest use of our land and water resources, protecting our fish and wildlife, preserving the environmental and cultural values of our national parks and historical places, and providing for the enjoyment of life through outdoor recreation. The Department assesses our energy and mineral resources and works to assure that their development is in the best interests of all our people. The Department also has a major responsibility for American Indian reservation communities and for people who live in Island Territories under U.S. administration.

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

A/m^2	ampere per square meter	pct	percent
atm	atmosphere	psi	pound per square inch
° C	degree Centigrade	psig	pound per square inch, gage
gpl	gram per liter	tpd	ton per day
hr	hour	tpy	ton per year
in	inch		
kg	kilogram		
lb	pound		

UPDATED PROCESS FLOWSHEETS FOR MANGANESE NODULE PROCESSING

By Benjamin W. Haynes,[1] Stephen L. Law,[2] and Riki Maeda[3]

ABSTRACT

The Bureau of Mines, in cooperation with the National Oceanic and Atmospheric Administration (NOAA), has updated a 1977 NOAA report prepared by Dames & Moore entitled, "Description of Manganese Nodule Processing Activities for Environmental Studies." This updated report contains detailed flowsheets and descriptions of the five potential first-generation nodule recovery schemes now considered most likely to be used by industry; they are high-temperature gas reduction and ammoniacal leach, Cuprion ammoniacal leach, high-temperature and high-pressure H_2SO_4 leach, reduction and HCl leach, and smelting and H_2SO_4 leach. The first three processes are three-metal recovery schemes (Cu, Ni, and Co) with the option of Mn recovery from the tailings. The remaining two processes are four-metal (Cu, Ni, Co, and Mn) recovery schemes.

All except the HCl process are assumed to use a nodule feed rate of 3 million tons per year (dry basis). Final metal products are Co powder and cathode Cu and Ni. A minor amount of Ni is also recovered as powder, and some Cu and Zn are recovered as mixed sulfides. Manganese in the four-metal processes is recovered as either manganese metal or ferromanganese.

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INTRODUCTION

This report is one in a series of reports issued by the Bureau of Mines as part of a research project entitled, "Analysis and Characterization of Potential Manganese Nodule Processing Rejects." Deep seabed mining for manganese nodules, including the processing of nodules to recover value metals, raises a variety of environmental, social, and economic considerations. To address the waste management aspects of the recovery of value metals from nodules, the National Oceanic and Atmospheric Administration (NOAA), U.S. Department of Commerce, the Environmental Protection Agency (EPA), and the Bureau of Mines and the Fish and Wildlife Service, U.S. Department of the Interior, after consultation with affected and concerned interests, have agreed to embark on a multiyear cooperative research program that has the following overall objective:

> "To provide information needed by Federal and State agencies in preparation for receipt of industry's commercial waste management plans."

The NOAA-funded research conducted by the Bureau of Mines has the objective of obtaining a first-order chemical and physical characterization of reject waste materials (tailings) from the types of manganese nodule processing techniques representative of those being developed by industry. The result of this research is expected to be a technical report that can be used by (1) environmental scientists in subsequent research to assess the potential effects of waste management alternatives, and (2) regulatory agencies in the determination of what standards and test requirements must be met. This is expected to facilitate the development of a basic framework that accommodates the desire to assure protection of the environment and the development of a new minerals processing industry.

In order to adequately assess the potential effects of disposing of reject waste materials from manganese nodule processing, appropriate process flowsheets must be developed so that the processes representative of first-generation nodule processing plants can be simulated and waste can be generated in the laboratory.

During August 1977, NOAA published a report prepared under contract by Dames & Moore entitled "Description of Manganese Nodule Processing Activities for Environmental Studies" *(7)*.[4] This report considered five different processing techniques or "roadmaps" (flowsheets). Three of these five, designed to produce Cu, Ni, and Co as primary products, are called "three-metal plants" and two are "four-metal plants" designed to produce manganese as a fourth primary product. It should be noted that three-metal plants could be designed to produce some manganese if market conditions are favorable. The processing techniques identified in the NOAA report are as follows:

1. Gas reduction and ammoniacal leach process.
2. Cuprion ammoniacal leach process.
3. High-temperature and high-pressure H_2SO_4 leach process.
4. Reduction and HCl leach process.
5. Smelting and H_2SO_4 leach process.

This Bureau of Mines report has taken the Dames & Moore 1977 flowsheets and used the input from industrial and other concerned parties to update the report and present, where necessary, changes and modifications in the flowsheets.

The flowsheets presented in this report are adaptations of the original flowsheets presented in reference 7. Only minor changes have been made in the sections common to all flowsheets. All flowsheets, however, are presented for completeness. This report, unlike the 1977 study, contains no energy balance or material balance figures. These flowsheets were used to design, construct, and operate bench-scale systems to generate reject waste materials. Reject waste materials are being generated and will be characterized to determine chemical and physical parameters important to future environmental and economic considerations. The results of the characterizations will be published in a separate report.

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MANGANESE NODULE PROCESSING OVERVIEW

GENERIC TYPES OF PROCESSES

In the work performed by Dames & Moore in 1977 *(7)*, a literature search revealed several methods for recovering the valued metals (Mn, Ni, Co, Cu) from manganese nodules using pyrometallurgical and hydrometallurgical processes, or combinations of the two. Furthermore, the extraction techniques can be classified by the type of lixiviant used to solubilize the metals of interest. These lixiviant types are ammonia-, chloride-, and sulfate-based. Using this format, Dames & Moore outlines 12 potential routes to metals recovery. These routes are

Ammoniacal systems

1. Gas reduction and ammoniacal leach

[4]Italicized numbers in parentheses refer to items in the list of references preceding the appendixes.

2. Cuprion ammoniacal leach
3. High-temperature ammonia leach

Chloride systems

1. Reduction and HCl leach
2. Hydrogen chloride reduction roast and acid leach
3. Segregation roast
4. Molten salt chlorination

Sulfate systems

1. High-temperature and high-pressure H_2SO_4 leach
2. Smelting and H_2SO_4 leach
3. H_2SO_4 reduction leach
4. Reduction roast and H_2SO_4 leach
5. Sulfation roast

Ammoniacal systems are used in processing of land-based nickeliferous laterites which are, in some respects, similar to manganese nodules. It is well known that Cu, Ni, and Co are soluble in ammoniacal ammonium carbonate (Caron process) and ammonium sulfate solutions. These processing routes involve selective reduction of the metals from their oxide states and disruption of the manganese nodule matrix to permit rapid, complete dissolution of the valuable metals.

Acid chloride solutions are also capable of solubilizing the metal values of interest including manganese, and a substantial body of literature exists describing process conditions for nodule reduction and metals recovery, separation, and purification.

Copper, nickel, and cobalt are also soluble in strong acid sulfate systems and serve as the initial step for various possible process routes. The high-temperature H_2SO_4 leach process technology is used in recovering nickel from laterites, where the high temperature increases the rates of the dissolution of Cu, Ni, and Co, and limits the solubility of undesirable compounds such as Fe and Mn. Alternative routes involving the acid sulfate lixiviant system include the selective, high-temperature reduction of the nodules, separation of manganese-rich slags from the metallic phases, sulfidation of metallic phases, and subsequent selective leaching of the sulfide materials. A ferromanganese product could also be recovered by further selective reduction of the manganese-rich slag phases.

PROCESSES MOST LIKELY FOR FIRST-GENERATION COMMERCIAL USE

Of the 12 generic process types presented previously, 7 have sufficient technical problems to preclude the likelihood of commercial development. Flowsheets have been developed for the five process options that are considered as first-generation choices, both from the published literature and by analogy to the processing of land-based ores *(7)*. These five process options are as follows:

1. Gas reduction and ammoniacal leach.
2. Cuprion ammoniacal leach.
3. High-temperature and high-pressure H_2SO_4 acid leach.
4. Reduction and HCl leach.
5. Smelting and H_2SO_4 leach.

The five processes can be broken down into three-metal and four-metal recovery systems with the three-metal systems having an option to recover manganese from the tailings. The basic three-metal systems are (1) gas reduction and ammoniacal leach process, (2) Cuprion ammoniacal leach process, and (3) high-temperature and high-pressure H_2SO_4 leach process. The remaining two are considered four-metal processes.

The recovery of manganese from the tailings of the three-metal systems involves two basic types of treatment. For the ammoniacal leach tailings, manganese can be recovered to a limited extent by the flotation of $MnCO_3$. The $MnCO_3$ could then be further processed to produce a manganese oxide product and sold as such or further processed to produce ferromanganese or other manganese alloys.

The residue from the H_2SO_4 system would require dissolution of the tailings and subsequent chemical manipulation to recover the manganese as MnO_2 or another form. The oxide product could be separated and sold or further processed to make ferromanganese or other manganese alloys. The possible direct use of the tailings from either the ammonia-based systems or the H_2SO_4 system as a feed for ferromanganese production would require some purification of the tailings. Trace metals levels as well as sulfur and possibly phosphorus levels would be too high for direct processing of the tailings by conventional methods.

For the purpose of this report, the add-on options to produce manganese products (ferromanganese, silicomanganese, and/or other oxide products) from the three-metal systems will be presented briefly with no process outlines. The proposed descriptions serve only as choices from several possible alternatives and, implementation or serious consideration would be dependent on many conditions in addition to technical feasibility.

SUMMARY PROCESS DESCRIPTIONS

This section contains brief descriptions of each of the five processes as mentioned in the preceding section along with block diagrams for each process. Detailed process descriptions of each process are given in the appendixes.

GAS REDUCTION AND AMMONIACAL LEACH PROCESS

Copper, nickel, and cobalt can be recovered from nodules by a process involving carbon monoxide gas reduction followed by an ammoniacal leach process. A simplified block diagram for this process is shown in figure 1.

The first step in this process is the high-temperature (625° C) reduction of manganese dioxide (MnO_2), the major compound in nodules, to manganese oxide (MnO) by a carbon monoxide-rich producer gas. The effect of this reduction is to disrupt the mineral structure and release the contained metals. The metal values solubilized are dissolved from the reduced nodules with a strong aqueous solution of ammonia (10 pct) and carbon dioxide (5 pct), at low temperature (40° C) and atmospheric pressure.

The metal-bearing solution is decanted from the nodules and treated with a series of organic extraction steps, which selectively remove the copper and nickel from the aqueous solution. The metal values are selectively stripped from the organic extract with acidified aqueous solutions. The metal products, copper and nickel, are produced from these acidic solutions by electrowinning.

Cobalt is then recovered from the aqueous ammonia-carbon

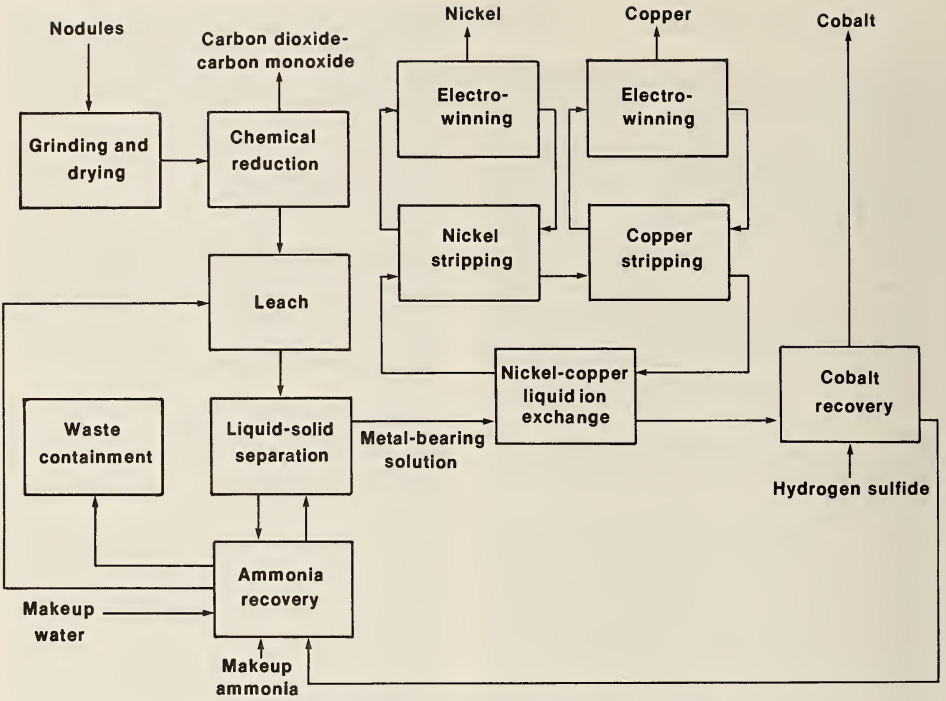

Figure 1.—Gas reduction and ammoniacal leach process.

dioxide solution by contacting it with hydrogen sulfide, which precipitates the insoluble sulfides of Co as well as small amounts of residual Cu, Ni, Zn, and other metals not removed in previous steps. The solids are removed from the aqueous ammonia-carbon dioxide solution and contacted with air and hot (100° C) H_2SO_4 to selectively redissolve the cobalt and the small amount of nickel present. The undissolved sulfides are sold as minor products, and the cobalt and nickel are recovered from solution in powder form by selective reduction with hydrogen at high pressure (34 atm) and temperature (185° C).

The nodule residue, from which the major portion (98 pct) of the soluble metals has been removed, is contacted with steam (at 120° C, 2 atm) to remove residual ammonia and carbon dioxide. The ammonia-carbon dioxide-steam mixture is condensed and, together with the aqueous ammonia-carbon dioxide mixture from which cobalt was removed, is recycled to extract more metal values from freshly reduced nodules. The steam-stripped nodule residues may be combined with smaller amounts of other process solid and liquid wastes and sent to containment.

The high-temperature reduction of nodules with simulated producer gases and subsequent extraction of metals with ammonia-carbon dioxide solutions is basically the same approach as is currently used in recovering nickel from laterites by the Caron process, and can be considered a variation of currently available technology. The metal separation and purification scheme, however, is specific to nodules and is complicated by the chemical similarity of Cu, Ni, and Co.

Separation and purification of copper and nickel by selective extraction with organic compounds (liquid ion exchange reagents) is currently practiced in the extractive metallurgy of copper and nickel. However, in these cases the aqueous solutions contain primarily one metal, the others being treated as impurities, not products.

Cobalt recovery from precipitated mixtures of nickel and cobalt sulfides derived from laterites is also currently practiced. The details of the procedures used to purify the leach solutions prior to reduction, however, would differ somewhat from those used for nodules because of the differences in amount and content of impurities.

Plant services include facilities for generating the producer gas used in nodule reduction, raising the necessary steam and part of the power required for process use, supplying the makeup and cooling water required, and providing for materials handling for process materials and supplies. The generation of producer gases from coal or oil for the reduction of nodules and all other plant services represent the utilization of known technology essentially without adaptation.

CUPRION AMMONIACAL LEACH PROCESS

Copper, nickel, and cobalt can be recovered from nodules by the Cuprion process employing a reducing ammoniacal leach. A simplified block diagram of this process is shown in figure 2.

The first step in this process is a low-temperature (50° C) hydrometallurgical reduction of manganese dioxide (MnO_2), the major compound in nodules, to manganese oxide (MnO) by an aqueous ammoniacal solution containing an excess of cuprous ions (Cu^+). The effect of this reduction is to disrupt the mineral structure and release the contained metals. The metal values are solubilized from the reduced nodules with a strong aqueous solution of ammonia and carbon dioxide at low temperature and pressure.

The metal-bearing solution is decanted from the nodules and treated with a series of organic extraction steps that selectively remove the copper and nickel from the aqueous solution. The metal values are in turn selectively stripped from the organic extract with acidified aqueous solutions. The metal products, cathode copper and nickel, are produced from these acidic solutions by electrowinning.

Cobalt is then recovered from the aqueous ammonia-carbon dioxide solution by precipitation with hydrogen sulfide, which also precipitates small amounts of residual Cu, Ni, Zn, and other metals not removed in previous steps. The solids are removed from the aqueous ammonia-carbon dioxide solution and contacted with air and hot (100° C) H_2SO_4 to selectively redissolve the cobalt and small amount of nickel present. The undissolved sulfides are sold as minor products, and the cobalt and nickel are recovered from solution in powder form by selective reduction with hydrogen at high pressure (34 atm) and temperature (185° C).

The nodule residue, which has the major portion (98 pct) of the soluble value metals removed, is contacted with steam (at 120° C, 2 atm pressure) to remove residual ammonia and carbon dioxide. The aqueous ammonia-carbon dioxide mixture, from which cobalt was removed, is also steam stripped to recover a high-strength ammonia solution for recycle to the reduction step and to provide fresh wash solution for recycle to extract more metal values from freshly reduced nodules. The steam-stripped nodule residues may be combined with smaller amounts of other process solid and liquid wastes and sent to containment.

The hydrometallurgical reduction of nodules in an ammoniacal-ammonium carbonate solution has been disclosed in the patent literature. While this approach differs from the pyrometallurgical reductions used in the well-known Caron process for recovering nickel from laterites, the basic outline for the Cuprion process is similar. The metal separation and purification scheme, however, is specific to nodules and is complicated by the chemical similarity of Cu, Ni, and Co.

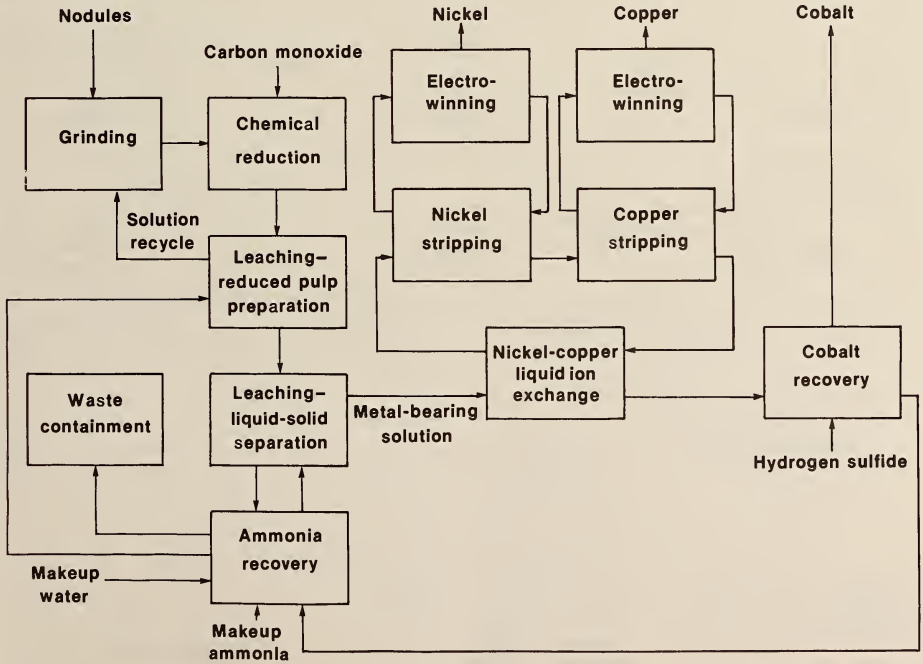

Figure 2.—Cuprion ammoniacal leach process.

Separation and purification of copper and nickel by selective extraction with organic compounds (liquid ion exchange reagents) is currently practiced in the extractive metallurgy of copper and nickel. However, in these cases the aqueous solutions contain primarily one metal, the others being treated as impurities, not products.

Cobalt recovery from precipitated mixtures of nickel and cobalt sulfides derived from laterites is also currently practiced. The details of the procedure used to purify the leach solutions prior to cobalt recovery will differ somewhat from those used for nodules because of the differences in amount and content of impurities. Also, the requirement that the nodule reduction and wash steps be carried out with solutions of differing ammonia and ammonium carbonate compositions requires an additional step, raffinate stripping, not used in the pyrometallurgical reduction-ammoniacal leach process.

Plant services include facilities for generating the carbon monoxide gas used in nodule reduction, raising the necessary steam and power required for process use, supplying the makeup and cooling water required, and providing for materials-handling for process materials and supplies. The generation of carbon monoxide gas from coal or oil for the reduction of cupric ion (Cu^{2+}) and all other plant services represent the utilization of known technology essentially without adaptation.

HIGH-TEMPERATURE AND HIGH-PRESSURE H_2SO_4 LEACH PROCESS

Nickel, copper, and cobalt can be recovered from nodules at high temperatures and high pressures in an aqueous H_2SO_4 solution. A simplified block diagram of this process is shown in figure 3.

The first step in this process is a high-temperature (245° C) and high-pressure (35 atm) treatment of the ground nodules. Most of the major metals of value in the nodules (except manganese) become dissolved in the hot, strong (30 pct) sulfuric acid solution. Iron is not solubilized to any appreciable extent. After cooling, the nodule residue and acid solution are separated by decantation. Water is used to wash the residue free of acid and soluble metals and it is then combined with the acid solution; the residue is sent to a containment area.

The metal-bearing acid solution passes to a pH-adjustment step prior to copper and nickel extraction. Copper and nickel are then removed from the solution with an organic extractant. The extracted nickel and copper are separately and selectively stripped from their respective organic extracts and transferred to acidified aqueous solutions, which accumulate nickel and copper sulfate, respectively. The metal products, cathode

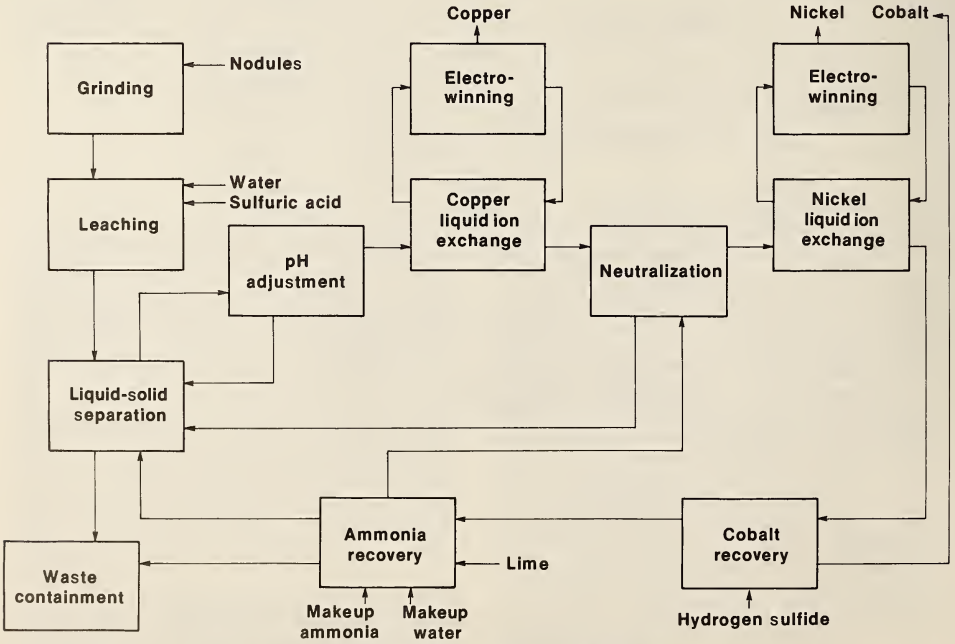

Figure 3.—High-temperature and high-pressure H_2SO_4 leach process.

nickel and copper, are produced from these acidic solutions by electrowinning.

Cobalt is then recovered by precipitation with hydrogen sulfide, which also precipitates small amounts of residual Cu, Ni, Zn, and other metals not removed in the previous steps. The solid residue is removed from solution and contacted with air and hot (100° C) H_2SO_4 to selectively redissolve the cobalt and the small amount of nickel present. The undissolved sulfides are sold as minor products, and the cobalt and nickel are recovered from solution in powder form by selective metal reduction through use of hydrogen gas at high pressure (34 atm) and temperature (185° C).

The solution, depleted of Cu, Ni, and Co, is chemically treated to recover the ammonia introduced during the neutralization step. The recovered ammonia is recycled for use in the process, and the ammonia-free solution is returned to wash freshly leached nodules.

Descriptions of high-temperature and high-pressure acid treatment of nodules have had limited exposure in the literature, with most descriptions occurring in foreign patents and papers. A basically similar process for treatment of nickel laterite ores has been used at Moa Bay, Cuba. The configuration proposed is an update using currently available technology of Moa Bay operations. The metal separation and purification scheme, however, is specific to nodules and is complicated by the chemical similarity of Cu, Ni, and Co.

Separation and purification of copper and nickel by selective extraction with organic compounds (liquid ion exchange reagents) is currently practiced in the extractive metallurgy of nickel and copper. However, in these cases the aqueous solutions contain primarily one metal, the others being treated as impurities, not products.

Cobalt recovery from precipitated mixtures of nickel and cobalt reduction differ somewhat from those used for nodules because of the differences in amount and content of impurities.

Plant services include facilities for generating the necessary steam and part of the power required for process use, for supplying the makeup and cooling water required, and for providing materials handling for process materials and supplies. The generation of steam and all other plant services represent the utilization of known technology essentially without adaptation.

REDUCTION AND HCl LEACH PROCESS

Copper, nickel, cobalt, and manganese can be recovered from nodules by a reduction and HCl leach process. A simplified block diagram of the process is shown in figure 4.

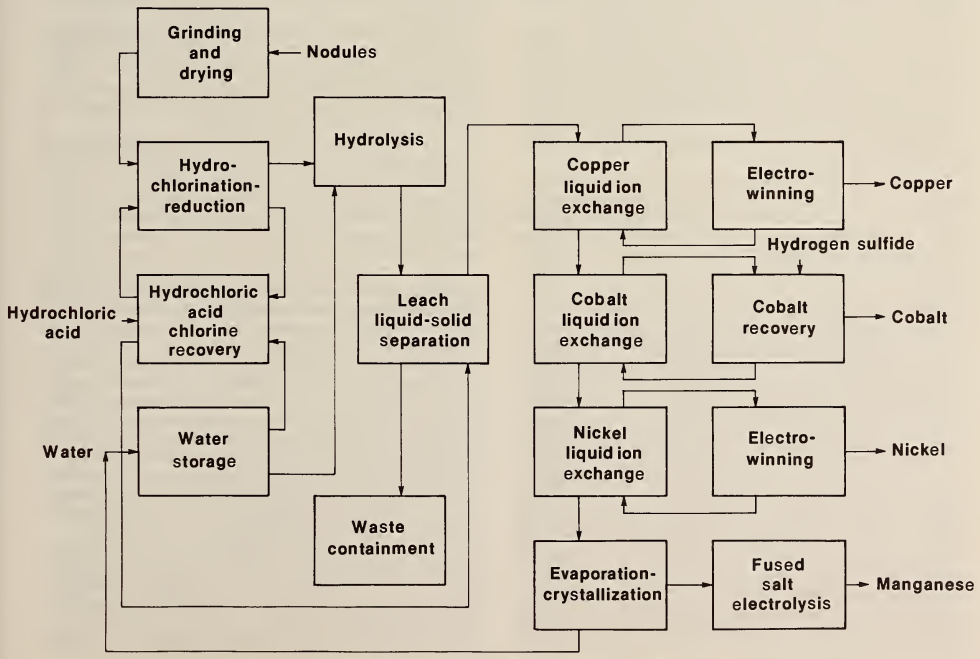

Figure 4.—Reduction and HCl leach process.

The chemical basis of the HCl process is the reduction of the manganese dioxide nodule matrix with hydrogen chloride to yield soluble manganese chloride, thereby releasing the Ni, Cu, and Co for dissolution. A portion of the hydrogen chloride is oxidized to chlorine, and the unreacted hydrogen chloride is separated from the accompanying chlorine and water vapor for recycling. Separation is accomplished by absorption of gasous HCl in concentrated HCl, in which chlorine has very limited solubility. The remaining chlorine gas is dried by passage through concentrated H_2SO_4.

Extensive solubilization of the iron content of the nodules during the initial high-temperature (500° C) reaction with gaseous hydrogen chloride is prevented by injection of steam. This results in the conversion (hydrolysis) of the iron chloride produced in the initial step to insoluble iron (ferric) hydroxide, simplifying subsequent metals separation and minimizing HCl regeneration requirements. In the next step, the soluble metal chlorides, particularly those of Mn, Ni, Cu, and Co, are brought into solution with water and aqueous HCl. In this process, as distinct from the other nodule treatment processes, the major metals separation steps are carried out from the chloride solution.

In the base-case process, copper is selectively extracted from the pregnant leach liquor by contact with an organic liquid ion exchange reagent. After separation of the copper-loaded organic phase from the copper-depleted aqueous chloride solution, the copper is stripped into a strong H_2SO_4 solution. The resulting copper sulfate solution is sent to electrowinning, producing cathode copper for sale and a partially copper-depleted, strong H_2SO_4 "spent" electrolyte that is returned to the liquid ion exchange circuit to strip more copper.

The chloride leach solution from which the copper has been removed is neutralized and passed to a solvent extraction step, where a different organic liquid ion exchange reagent selectively removes the cobalt from solution. The cobalt is recovered in a sequence of steps that includes stripping from the organic solvent, hydrogen sulfide precipitation as cobalt sulfide, selective leaching, and hydrogen reduction to cobalt powder.

The copper- and cobalt-depleted solution is next sent to a liquid ion exchange circuit where nickel is selectively separated from the solution and stripped into an acidic sulfate solution for nickel electrowinning. The nickel separation has many features in common with copper separation, except that much lower acid concentrations are appropriate in the case of nickel.

Of the several options for manganese recovery from nodules, that selected for the base-case process in this report involves drying of the final aqueous chloride solution to produce a dry, impure manganese chloride. The manganese chloride is charged to a high-temperature electrolysis furnace, where it dissolves in a molten alkali chloride bath. Electrolysis of the bath liberates molten manganese, which is tapped from the furnace, cast into molds, and sold as manganese metal. Fused salt impurities are skimmed off, solidified, and sent to waste disposal.

The second major product of the electrolysis is chlorine gas, which would be recovered along with the chlorine produced in the initial hydrochlorination step. The recovered chlorine needs to be reconverted to hydrogen chloride or otherwise utilized offsite in a large-scale chemical process, such as the manufacture of polyvinyl chloride.

Plant services include facilities for raising the necessary steam and part of the power required for process use, supplying the makeup and cooling water required, and providing for materials handling for process materials and supplies. The generation of steam and all other plant services represent the utilization of known technology essentially without adaptation.

SMELTING AND H_2SO_4 LEACH PROCESS

Copper, nickel, cobalt, and a ferromanganese alloy, if desired, can be recovered from nodules by a smelting and H_2SO_4 leach process. A simplified block diagram of this process is shown in figure 5.

The nodules are first dried by direct contact with combustion gases to remove water not chemically bound to the minerals. The manganese dioxide and ferric oxide are then reduced to manganous and ferrous oxides by contact, in the presence of coal, with a carbon monoxide-rich producer gas at high temperature (>625° C up to 1,000° C). The hot, reduced nodules are then charged to an electric furnace, along with the coke and silica. In this step most of the Cu, Ni, Co, and Fe and some of the Mn are reduced (at 1,425° C) and form a molten alloy phase, which separates by gravity from the unreduced manganese slag.

The hot alloy is transferred to converter vessels where, with additional silica, the manganese and most of the iron are re-oxidized with air, separated as a slag, and returned to the electric furnace. Gypsum and coke or possibly sulfur are then added to the alloy, producing a metal sulfide "matte" phase that contains the Cu, Ni, and Co. A second liquid-liquid separation is made in the converter, with the slag returned to the electric furnace and the matte granulated by quenching it in cold water.

The electric furnace manganese slag, with recycled iron-rich slags, may be further reduced (at 1,480° C) with additional coke in an electric furnace to produce a molten ferromanganese alloy, which separates by gravity from the unreduced manganese slag. The ferromanganese is cast for sale, and the waste slag is granulated for disposal.

The metals are recovered from the granulated matte by dissolution into strong (5 pct), hot (110° C) H_2SO_4 solution in the presence of oxygen (at 10 atm pressure). The metal-bearing solution is treated by a series of purification steps in which it is contacted with an organic extractant that selectively removes the copper and nickel from the aqueous solution. Ammonia is added to the solution to control the pH during the separations. The metal values are, in turn, selectively removed from the organic extract and transferred to acidified aqueous solutions, which accumulate copper and nickel sulfates. The metal products, cathode copper and nickel, are produced from these acidic solutions by electrowinning.

Cobalt and small amounts of copper, nickel, and other metals not removed in previous steps are recovered from the aqueous ammonium sulfate solutions by hydrogen sulfide precipitation. The solids are removed from the aqueous ammonium sulfate solution and contacted with air and hot (100° C) H_2SO_4 to selectively redissolve the cobalt and the small amount of nickel present. The undissolved sulfides are sold as minor products, and the cobalt and nickel are recovered from solution in powder form by selective reduction with hydrogen at high pressure (34 atm) and temperature (185° C).

Lime is then added to the metal-free ammonium sulfate solution, and the mixture is contacted with steam (at 120° C, 2 atm) to recover ammonia for reuse in the process. The gypsum formed in this step is combined with other process solid and liquid wastes and sent to containment.

While detailed design information on the process implica-

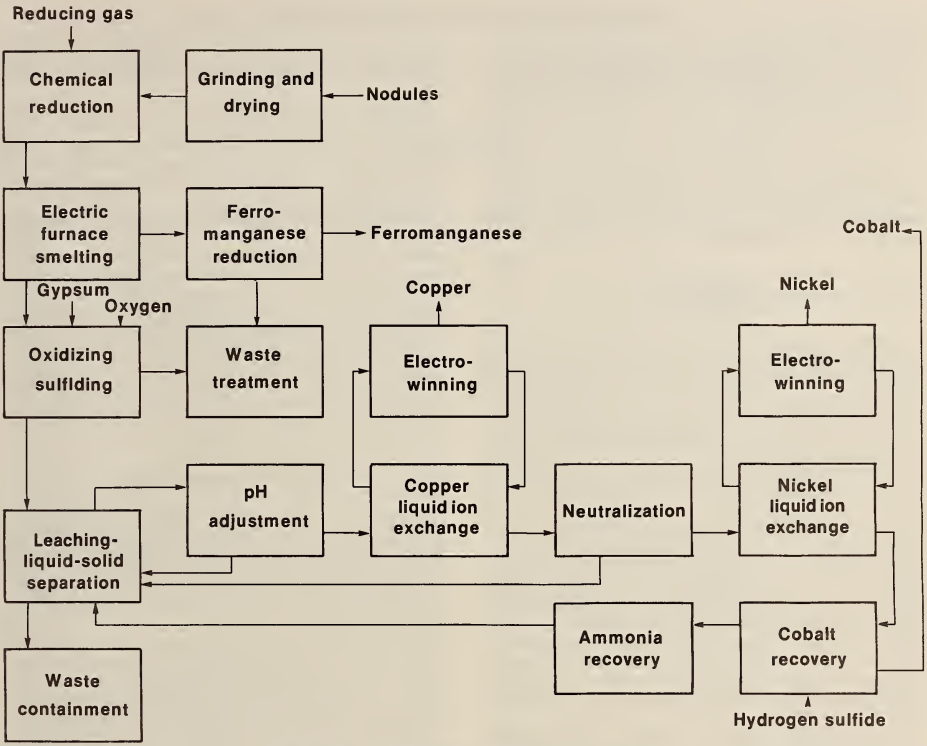

Figure 5.—Smelting and H_2SO_4 leach process.

tions involved in the smelting of nodules has not been published, enough is known about the thermodynamics of the system to permit a process outline to be constructed. Electric furnace smelting is a well developed technology, and copper and nickel are currently recovered by treatment of mattes formed during the smelting of sulfide ores. Ferromanganese of high purity is currently produced directly from high-quality ores. Thus, the reductive smelting of nodules to ferromanganese with subsequent sulfidizing of the alloy phase to form a matte is a synthesis of technologies from different areas of extractive metallurgy. Detailed information on slag properties (particularly viscosity-composition-temperature relationships); the efficiencies of materials (coke, gypsum); energy consumption; and the distribution of minor metals and impurities among dust, slag, and matte phases under smelting conditions for this system, however, is lacking.

The oxidative dissolution of sulfide ores and mattes is well known, but the metal separation and purification schemes are specific to nodules and are complicated by the chemical similarity of Cu, Ni, and Co. Separation and purification of copper and nickel by selective extraction with organic compounds (liquid ion exchange reagents) is currently practiced in the extractive metallurgy of copper and nickel. However, in these cases the aqueous solutions contain primarily one metal, the others being treated as impurities, not products.

Cobalt recovery from precipitated mixtures of nickel and cobalt sulfides derived from laterites is also currently practiced. The details of the procedures used to purify the leach solutions prior to reduction will differ somewhat from those used for nodules because of the difference in amount and content of impurities.

Plant services include facilities for generating the producer gas used in nodule reduction, generating the necessary steam and part of the power required for process use, supplying the makeup and cooling water required, and providing for materials handling for process materials and supplies. The generation of producer gases from coal (or oil) for the reduction of nodules and all other plant services represent the utilization of known technology essentially without adaptation.

DETAILED PROCESS DESCRIPTIONS

Each of the five processes are presented in detail, in the appendixes, with flowsheets for each unit operation. Many sections of the processes are similiar or identical but flowsheets are presented to preserve the process continuity. Major assumptions used in calculating operating parameters are presented to show major changes from the Dames & Moore 1977 report *(7)*. Materials handling for all processes is similar and is presented prior to the detailed process descriptions without flowsheets. Plant services are presented without flowsheets for each of the five processes.

MAJOR ASSUMPTIONS

Certain assumptions were used in the original Dames & Moore report and are used in updating the process flowsheets in this report. The three three-metal processes and the smelting process are assumed to operate on a 3-million-tpy feed rate (dry basis). The four-metal HCl process is assumed to operate at 1 million tpy (dry basis). The final products are assumed to be Cu and Ni cathodes, some Ni powder, Co powder, small amounts of Cu and Zn sulfides, Mn metal, and ferromanganese. No energy balances or material balances are made in this report.

Several significant changes from the Dames & Moore report are detailed here. In the 1977 Dames & Moore study *(7)*, a moisture content of 37.5 pct was used as the water value of nodules fed to the processing plant. This value represents essentially the water content of as-mined nodules. Considering the porosity of nodules (60 pct), it is likely that a substantial amount of water will be removed during transport from the mine site. Ships currently in use equipped with a Marconoflo-type[5] dewatering system should be able to dewater the nodules. A recent report described the use of such a system in transporting slurried coal *(30)*.

A more reasonable value for moisture content of nodules received at the port facilities may be 15 to 20 pct. This fact would decrease the size of several components of the materials handling section, and lower the energy cost for drying the nodules. For this report a moisture content of 20 pct is used for nodules fed to the plant. This lowers the 3-million-tpy (dry-basis) plant feed rate from 12,500 to 10,900 tpd, and the 1-million-tpy (dry-basis) plant feed rate from 3,750 to 3,640 tpd.

A second major change from the 1977 study *(7)* is the increase in size of the smelting plant from 1 million tpy (dry basis) to 3 million tpy (dry-basis) to allow use of conventionally sized furnaces. Also, particle size of the nodule feed is increased to minus 65 mesh instead of minus 200 or minus 325 mesh as previously used.

The previous study contained an extensive bibliography and it will not be duplicated in this report. However, certain pertinent publications since 1977 are included in the reference section of this report *(1-6, 8-29, 31-32)*. Certain publications apply directly to one or two processes, while others are more general in nature. Updated details of the Cuprion process *(1-3, 20, 26)* and modifications of the Caron process *(5, 9-12, 24-25, 32)* have been published. Several articles on different aspects of H_2SO_4 leaching of laterites and nodules *(6, 8, 10, 18, 23)* are available as well as those dealing with smelting processes *(13, 21-22, 29, 31-32)*. Several review articles have also been published *(4, 14, 17, 27-28)*.

MATERIALS HANDLING

Facilities are provided within the plant for receiving and reclaiming raw nodules, coal, lime and limestone, ammonia, other process materials, and fuel. Provisions for handling hydrogen chloride and chlorine are also required for the reduction and HCl process, and provisions for handling silica, gypsum, and acids are made for the smelting and H_2SO_4 process. In the 1977 Dames & Moore study *(7)*, the proposed method of nodule transport from the port facilities was a slurry pipeline. Assuming nodules can be dewatered to 15 to 20 pct moisture, the use of slurry pipelines may not be cost effective. At this moisture content, the use of conveyors for transport appears more likely. Conveyors are routinely used in mining industries to transport materials over both long and short distances in many areas. The use of conveyors for nodule transport would involve known technology with little adaptation. Because all processes (except Cuprion) require the water associated with nodules to be completely removed, the use of dewatering during ship transport, coupled with conveyor transport, should result in an overall net energy savings.

SUMMARY

This report is an update of the 1977 study *(7)* by Dames & Moore and EIC Corporation entitled, "Description of Manganese Nodule Processing Activities for Enviromental Studies," but does not include the energy and material balances contained in the initial study. The flowsheets presented in the appendixes of this report are adaptations of those in the previous report with the changes since 1977. The five manganese nodule processing options outlined in this report are gas reduction and ammoniacal leach process, Cuprion ammonical leach process, high-temperature and high-pressure H_2SO_4 leach process, reduction and HCl leach process, and smelting and H_2SO_4 leach process. The first three processes are designed to recover three metals (Cu, Co, and Ni), and the latter two are designed to recover four metals (Cu, Co, Ni, and Mn). The three-metal processes have the option of recovering manganese from the tailings if economically feasible.

This report differs from the 1977 study *(7)* by using a larger mesh size of minus 65 for the feed material for all processes except smelting (where minimal size reduction is required); by using a moisture content of 20 pct rather than 37.5 pct for the feed nodules; by upgrading the smelting process to a 3-million-tpy nodule feed rate (dry basis) to allow for more conventionally sized furnaces; and by recognizing the use of dewatering of the nodules during ship transport, coupled with conveyors instead of slurry pipeline transport of nodules from the port to the plant.

[5]Reference to specific trade names or equipment does not imply endorsement by the Bureau of Mines.

A summary table of operating parameters is presented for each of the five processes and each process is broken down into basic unit operations (e.g., grinding, leaching, solid-liquid separation, solvent extraction, electrowinning, etc.). Each process may be examined as a complete package, containing detailed flowsheets and process descriptions pertaining to that process, even though portions of one process may be identical to similiar segments of other processes.

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APPENDIX A.—GAS REDUCTION AND AMMONIACAL LEACH PROCESS

The gas reduction and ammoniacal leach process is a three-metal process in which Cu, Ni, and Co are liberated by an oxidizing ammoniacal-ammonium carbonate leach following the high-temperature reduction of manganese dioxide by a synthesis gas. Copper and nickel are coextracted by liquid ion exchange (LIX) reagents and are selectively stripped and recovered as electrowon cathodes. Cobalt is separated from the raffinate by precipitation with hydrogen sulfide and is recovered from the sulfide precipitate along with some Ni, Zn, and Cu, by selective leaching and hydrogen reduction. The metal-free raffinate is recycled to provide leach liquor and to wash the process tailings. Ammonia and ammonium carbonate are recovered from leach tailings by steam stripping.

Detailed descriptions of each segment of the process are given for the following flowsheets. A summary of operating parameters for each section is given in table A-1. A key to the flowsheet symbols is given in figure A-1.

ORE PROCESSING AND DRYING (FIG. A-2)

Wet nodules are reclaimed from storage and fed through a primary cage mill where they are reduced to minus ⅞ in. They then pass to a fluid bed dryer where surface and pore water is removed at 175° C by direct contact drying with combustion gases. Bed overflow is reduced to minus 65 mesh in a secondary cage mill, and dryer and mill fines are removed from offgases with cyclones and an electrostatic precipitator. Offgases pass to gas treatment for scrubbing, while dried nodules are transferred hot in a covered conveyor to reduction.

REDUCTION (FIG. A-3)

Dried nodules are reduced at 625° C in a two-stage fluid bed reduction roaster by contact with producer gas derived from coal gasification. At reduction conditions, MnO_2 as well as Cu, Co, Ni, Fe, and Zn are reduced. The carbon dioxide-rich offgases are cooled in waste heat recovery and used to carbonate the reduced manganese oxide, forming manganese carbonate in a fluid bed cooler at 125° C. The reduced, carbonated material is further cooled by a water spray in the fluid bed unit and quenched with recycle liquor in an agitated tank. Cooled offgases pass to dust removal and unutilized carbon monoxide and hydrogen pass to the main boilers for combustion.

LEACHING-AERATION (FIG. A-4)

The reduced nodule slurry passes to a countercurrent oxidizing leach where air is sparged into the leach slurry to oxidize Co^{2+} to Co^{3+} and Fe^{2+} to Fe^{3+} precipitating the Fe as insoluble ferric hydroxide in the manganese carbonate tailings. Liquid-solid separations are made in thickeners, which also provide residence time for leaching. Offgases from aeration pass to ammonia recovery, leached nodules to washing, and pregnant liquor to LIX for metal separation and purification.

SOLID-LIQUID SEPARATION (FIG. A-5)

Metal values that have been solubilized and absorbed on the tailings in leaching are recovered from the tailings by washing in a countercurrent decantation (CCD) circuit using covered thickeners. Wash liquor consists of recovered ammonia and ammonium carbonate along with raffinate from cobalt recovery. Washed tailings pass to stripping for ammonia and ammonium carbonate recovery while the wash overflow passes to leaching.

LIQUID ION EXCHANGE-EXTRACTION (FIG. A-6)

Pregnant liquor from leaching is filtered and passed to a three-stage, countercurrent LIX extraction circuit where copper, nickel, and some ammonia are removed from the pregnant liquor. Most of the ammonia is removed from the organic phase by washing with a weak aqueous ammonia solution. This ammonia is recovered by steam stripping a portion of the scrub solution, with the vapors passing to the ammonia recovery section. Provision is made for periodically cleaning the mixer-settler units used in extraction and stripping and for recovering organic and aqueous phases for recycle. Degraded organic, dust, and other forms of "crud" are removed from the organic and incinerated. Because a small amount of Co is coextracted and is not stripped with Cu and Ni, it must be removed from the LIX reagent to prevent its buildup. This is accomplished by precipitating the cobalt, with hydrogen sulfide, from a purge stream of organic. The precipitated solids are washed from the organic and pass to cobalt recovery, while the purified organic is returned to the extraction circuit (fig. A-7).

LIQUID ION EXCHANGE-STRIPPING (FIG. A-8)

The remainder of the ammonia is removed from the loaded organic by washing with a slightly acidic ammonium sulfate solution. The ammonium sulfate formed in scrubbing is purged to ammonia recovery. Nickel is selectively stripped from the organic by countercurrent contact at controlled pH with depleted electrolyte from nickel electrowinning. Because electrowinning conventionally occurs at a higher temperature than operation of the LIX circuit, the strip solution is heated passing to electrowinning and cooled passing from electrowinning. Copper is then removed from the nickel-free organic by countercurrent stripping with depleted electrolyte from copper electrowinning. The copper electrolyte is also heated-cooled on passage to-from electrowinning to permit operation of electrowinning at a higher temperature. Makeup organic is added to the stripped reagent to offset degradation and soluble organic losses to the pregnant liquor, and the metal-free organic is recycled to extraction.

COPPER ELECTROWINNING—COMMERCIAL (FIG. A-9)

Cathode copper is recovered from the strong electrolyte from LIX using conventional technology. Starter sheets are deposited on titanium blanks from a strong electrolyte and are removed, washed, looped, and returned to the commerical section as starters. Full-term cathodes produced in the commercial section are washed, unloaded, and prepared for ship-

Table A-1.—Operating parameters for gas reduction and ammoniacal leach process

Parameter and unit	Value
ORE PROCESSING AND DRYING (FIG. A-2)	
Feed rate, wet basis (330 days/yr; 24 hr/day) ..... tpd..	10,900
Feed size to reduction ..... mesh..	−65
Drying temperature ..... ° C..	150
REDUCTION (FIG. A-3)	
Reductant gas composition, pct:	
CO	18.2
CO_2	7.8
H_2	10.9
N_2	49
H_2O	10.1
CH_4	3.6
Gas temperature ..... ° C..	825
Reduction temperature ..... ° C..	625
Mn carbonation ..... pct..	95
Cooling temperature ..... ° C..	125
Reduction reactions:	
$MnO_2 + CO \rightarrow MnO + CO_2$	
$Fe_2O_3 + CO \rightarrow 2FeO + CO_2$	
$NiO + CO \rightarrow Ni + CO_2$	
$CuO + CO \rightarrow Cu + CO_2$	
$CoO + CO \rightarrow Co + CO_2$	
Conversion, pct:	
Co	100
Cu	100
Fe	98
Mn	98
Ni	100
LEACHING-AERATION (FIG. A-4)	
Number of stages	3
Temperature ..... ° C..	40
Time per stage ..... hr..	1
Leach solution composition, gpl:	
NH_3	100
CO_2	50
Pressure ..... atm..	1
Solubilization of metals, pct:	
Co	70
Cu	90
Fe	≈1
Mn	≈1
Mo	80
Ni	90
Zn	40
SOLID-LIQUID SEPARATION (FIG. A-5)	
Underflow density ..... pct solids..	35 – 40
Wash ratio ..... kg/kg liquor..	2
Wash recovery ..... pct..	98
Wash liquor composition, gpl:	
NH_3	100
CO_2	50
LIQUID ION EXCHANGE-EXTRACTION (FIG. A-6)	
Extraction:	
Extractant	[1]LIX 64N
Number of stages	3
Organic-aqueous ratio	2:1
Metals extraction, pct:	
Co	1
Cu	99.9
Ni	99.9
Zn	10
Washing (primary):	
Washing agent ..... pct NH_3..	1
Number of stages	2
Organic-aqueous ratio	3:1
Residual NH_3 in organic ..... gpl..	0.1
LIQUID ION EXCHANGE-STRIPPING (FIG. A-8)	
Washing (secondary):	
Wash composition, gpl:	
$(NH_4)_2SO_4$	200
H_2SO_4	1

Parameter and unit	Value
LIQUID ION EXCHANGE-STRIPPING (FIG. A-8)—Con.	
Washing (secondary)—Con.	
Number of stages	2
Organic-aqueous ratio	1:1
Residual NH_3 in organic ..... gpl..	0.01
Ni stripping:	
Strip solution composition, gpl:	
Cu	<0.001
H_2SO_4	40
Ni	50
Zn	≈0
Number of stages	3
Organic-aqueous ratio	5:1
Stripping, pct:	
Co	0.3
Cu	<.004
Ni	98.8
Zn	≈0
Cu stripping:	
Strip solution composition, gpl:	
Cu	40
H_2SO_4	160
Ni (max)	10
Zn	5
Number of stages	2
Organic-aqueous ratio	3:1
Stripping, pct:	
Co	0.2
Cu	87
Ni	≈0
Zn	100
Temperature ..... ° C..	40
COPPER ELECTROWINNING—COMMERCIAL (FIG. A-9)	
Current density ..... A/m^2..	180
Current efficiency ..... pct..	94
Temperature ..... ° C..	50
Cu in-out ..... gpl..	53-40
H_2SO_4 in-out ..... gpl..	160-180
NICKEL ELECTROWINNING—COMMERCIAL (FIG. A-10)	
Current density ..... A/m^2..	180
Current efficiency ..... pct..	93
Temperature ..... ° C..	60
Ni in-out ..... gpl..	75-50
H_2SO_4 in-out ..... gpl..	0.016-40
Na_2SO_4 ..... gpl..	100
H_3BO_3 ..... gpl..	15
COBALT RECOVERY (FIG. A-11)	
Precipitating agent ..... pct NH_4HS..	30
Precipitation, pct:	
Co	98
Cu	99.9
Ni	99
Zn	99.9
Temperature ..... ° C..	80
Clarifier density ..... pct solids..	5
Wash ratio	2:1
Co leaching: slurry ..... pct..	40
Leaching agent ..... pct H_2SO_4..	70
Evaporation-crystallization water removal ..... pct..	70
Co oxidation:	
Temperature ..... ° C..	100
Pressure ..... psig..	150
Co reduction:	
Temperature ..... ° C..	175
Pressure ..... psig..	500
Reductant	H_2
AMMONIA RECOVERY (FIG. A-12)	
CO_2 absorber:	
Temperature ..... ° C..	40
Pressure ..... atm..	1.2
Efficiency for CO_2 ..... pct..	99
Number of stages	1

[1]Reference to specific trade names does not imply endorsement by the Bureau of Mines.

Table A-1.—Operating parameters for gas reduction and ammoniacal leach process—Continued

Parameter and unit	Value	Parameter and unit	Value
AMMONIA RECOVERY (FIG. A-12)—Con.		AMMONIA RECOVERY (FIG. A-12)—Con.	
NH_3 absorber:		NH_3 stripper:	
Temperature.....° C..	35	Pressure.....atm..	1.5
Pressure.....atm..	1.2	Recovery of NH_3.....pct..	99
Number of stages.....	1	Number of stages.....	2

ment to sale. The greater portion of the weak electrolyte is recycled to the LIX section for stripping. A small amount of nickel is stripped along with the copper not deposited in electrowinning, and must be purged from the system. The purged electrolyte passes through purification cells where copper is removed by electrowinning to depletion. The decopperized electrolyte passes to vacuum evaporators where water is removed and nickel sulfate is precipitated from the resulting highly acidic solution. The nickel sulfate is removed and sent to cobalt recovery where it is combined with other purge streams. The acid is returned to the process where, with makeup acid, it is used to dissolve scrap copper for return to the commercial cells for deposition. Sufficient steam, wash water, and makeup water are added to the circuit to offset water vaporized or carried off with evolved oxygen during electrowinning.

NICKEL ELECTROWINNING—COMMERICAL (FIG. A-10)

Nickel is recovered from the strong electrolyte by electrowinning in a manner similar to that used for copper recovery. In nickel electrowinning, however, cathode bags are used, and sodium sulfate and boric acid are added to the electrolyte to control its conductivity and pH. Dissolved organic carried from the LIX step is removed by adsorption on activated carbon prior to any electrolyte passing to electrowinning. Also, the starter sheets are pickled in H_2SO_4 prior to use in the commercial cells, and nickel scrap is dissolved in ammonia-containing raffinate and recycled to the pregnant liquor, rather than to the recycled or makeup acid solution. The electrolyte purge required to remove impurities from the electrowinning circuit passes to a sulfide precipitation reactor and then to cobalt recovery for recovery of metal values.

COBALT RECOVERY (FIG. A-11)

Along with unextracted Cu, Ni, and Zn, Co is recovered from the LIX raffinate by precipitation with ammonium hydrosulfide (produced by sparging hydrogen sulfide into an excess of ammonia solution). The sulfide precipitate is separated from the raffinate in a clarifier, with the clarifier overflow being recycled for tailings washing and the underflow passing to stripping for ammonia recovery.

The sulfide slurry is mixed with electrolyte purges from Cu and Ni electrowinning, and with Co recovered from stripping the LIX reagent. The mixture is pressure leached with air to preferentially dissolve the Ni and Co sulfides, leaving the Cu and Zn sulfides in the residues. The latter are removed by filtration and sold as minor products to smelters for recovery of metal values.

Following pH adjustment and reprecipitation with hydrogen sulfide for final removal of any Zn and Cu solubilized in the first leach, the Ni-Co sulfate solution is heated and autoclaved, and Ni is reduced with hydrogen. Sufficient ammonia solution is added during reduction to neutralize the acid formed. Only a portion of the nickel is removed per pass to prevent overreduction and subsequent contamination of the nickel powder with cobalt. After densification through repeated recycle, the nickel powder is removed, washed, and passed to drying and briquetting for sale.

The largely nickel-free cobalt sulfate solution passes to an evaporator-crystallizer where the remaining nickel and cobalt are precipitated as the double salts with ammonium sulfate. Excess ammonium sulfate is purged, and the salts are redissolved in strong ammonia solution. The cobalt in solution is oxidized to the cobaltic state (Co^{3+}) with air. This permits the cobalt to remain in solution when the stream is acidified to remove the nickel salts, which are separated and recycled to the pH adjustment step. The nickel-free solution is then heated and autoclaved for removal of cobalt by hydrogen reduction. Sufficient ammonia is added to neutralize the acid generated. The cobalt powder is dried and briquetted for sale, while the ammonium sulfate is purged to the ammonia recovery process.

AMMONIA RECOVERY (FIG. A-12)

Tailings from the CCD wash circuit are preheated and stripped for ammonia recovery by countercurrent contact with steam in stripping towers. The steam and ammonia vapors from stripping are combined with vapors from other ammonia strippers and pass to an ammonia absorber-condenser tower where most of the ammonia and ammonium carbonate are condensed. Vent gases pass to a carbon dioxide absorber where they are absorbed, along with the required makeup carbon dioxide obtained from boiler offgases, in makeup scrubbing water. Ammonia is recovered from all process vents by countercurrent contact with makeup scrubbing water in an ammonia absorber and vent scrubber. The ammonia-free gases pass to stacks for disposal.

Ammonia is recovered from the ammonium sulfate purges from cobalt recovery and the LIX washing step by reaction with slaked lime. Steam is blown into the mixture to strip the evolved ammonia, and the vapor is condensed. The condensate is returned to aqueous ammonia storage for recycle within the process. The gypsum slurry from the lime boil is cooled, along with the slurry from the tailings stripping, and passed to tailings surge. This is combined with process solid and liquid wastes and plant runoff, treated for pH control, as required, and pumped to the tailings impoundment area for disposal.

PLANT SERVICES

Plant services include process and cooling water supply and treatment, steam raising and power generation, gas treatment, and reducing gas preparation. Makeup water is clarified and softened for distribution to the process, as required. Additional treatment is required for cooling tower water makeup, boiler feed water makeup, and for supplying plant potable water. Offgases from manganese reduction are burned, along with additional coal, in the main boilers to raise the required process steam and generate a portion of the power required in the process. Following particulate removal, the flue gases are combined with other process offgases and pass to gas treatment, where sulfur oxides and other acidic constituents are removed by scrubbing with limestone. The scrubbed offgases are reheated, combined with scrubbed vents from ammonia recovery, and are passed to stacks for disposal. Gas for nodule reduction is produced in a two-stage entrained-flow gasifier in which coal is mixed with preheated air and high-temperature steam for the production of a carbon monoxide-rich reducing gas. The gasifier product passes to reduction following particulate removal and energy recovery, with sulfur removal taking place after combustion and with other boiler flue gases.

MANGANESE PRODUCTION ADD-ON

The recovery of manganese from ammoniacal leach tails is an option that has been investigated. Manganese may be partially recovered from tailings by flotation of the fine $MnCO_3$ present. The $MnCO_3$ could then be converted to an oxide form for feed to produce ferromanganese or other manganese alloys. The recovery of manganese from the process tails would be contingent on the market conditions and process economics. Some intermediary product may have market value, thereby avoiding energy-intensive steps to produce manganese alloys. Because of the relatively new technology required for manganese recovery from ammoniacal leach tails, and the dependency upon economics and technical conditions, no detailed flowsheets are presented for this process.

PROCESS ALTERNATIVES

A major processing alternative, involving the hydrometallurgical reduction-ammoniacal leaching of nodules is fully documented in appendix B.

Other than the metals separation and purification steps, the process configuration is based on the well-known Caron process, and there is little reason to believe, in the absence of actual operating data, that the fundamental approach should differ.

It has been assumed that the reduced nodules can be carbonated in a fluid bed cooler prior to leaching. If carbonation is not complete, the nodules would absorb carbon dioxide directly from the leach liquor. Then, to maintain the required pH, the wash liquor would have to be recycled with a higher ammonium carbonate content. This, in turn, would be obtained by scrubbing a much larger fraction of the boiler flue gases in the ammonia recovery section.

The use of fluid bed dryers and reactors represents an advance in processing technology over the use of rotary kilns and multiple hearth furnaces and should not drastically affect any material balance. It has been assumed that the leached tails can be stripped for ammonia recovery in the same way as is done in laterite processing, although unexpected fouling tendencies could require the use of less efficient stripping devices, thereby increasing steam (fuel) consumption.

The ammonium sulfate solutions purged from the liquid ion exchange-extraction and cobalt recovery sections have been treated with lime for the recovery of ammonia for recycle. An alternative approach would involve direct recovery of ammonium sulfate by evaporation-crystallization, for sale as a byproduct.

Alternative configurations of the metals separation steps are possible, such as selective extraction-selective stripping, but their impact on overall plant material and energy balances should be minor. Many variations are possible in the details of the scheme used for recovery of cobalt from a mixed sulfide precipitate. Ultimately, however, their impact on plant requirements would not differ greatly from the approach used here, because the sulfides will still be oxidized to sulfates, purged, and hydrogen reduced. It does not appear likely that solutions could be purified easily enough to permit recovery of electrolytic cobalt.

Absorber

Aerator

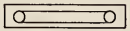
Agitator

Autoclave

Blower

Centrifuge

Conveyor



Covered conveyor

Cyclone

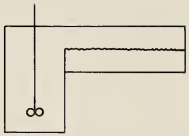
Ejector

Filter

Filter

Heat exchanger

Hopper

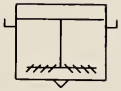


Mixer-settler

Pump

Surge tank

Surge tank, agitated



Thickener

Figure A-1.—Key to symbols.

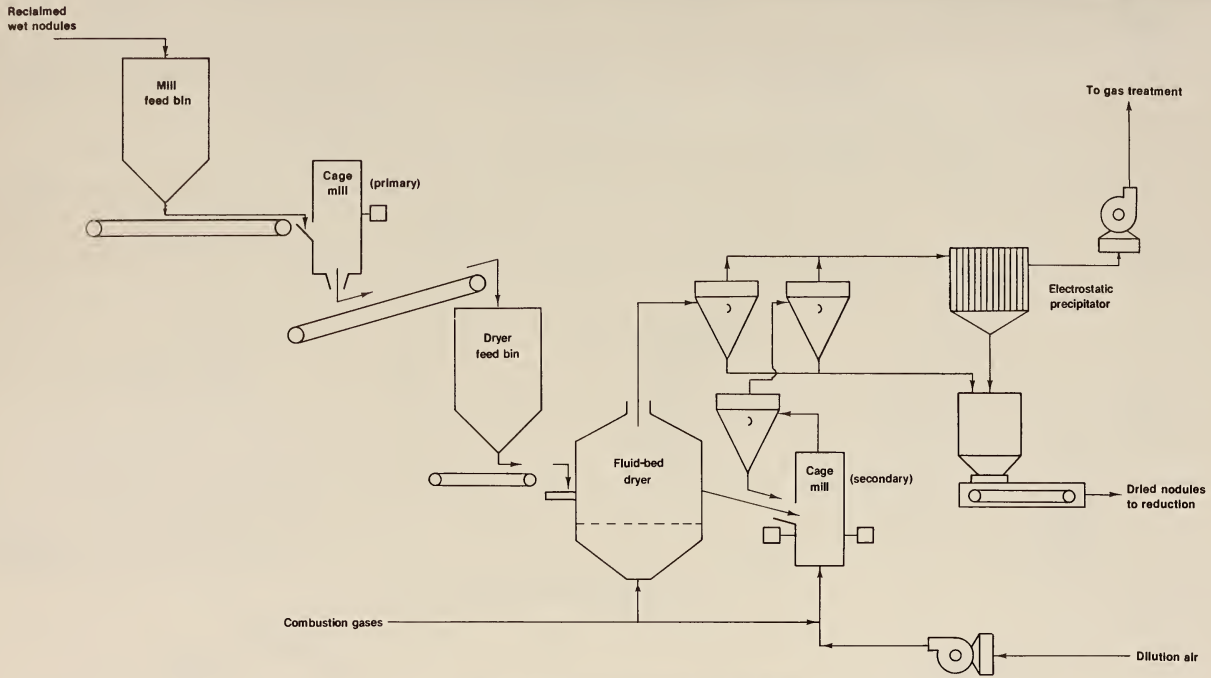


Figure A-2.—Ore processing and drying.

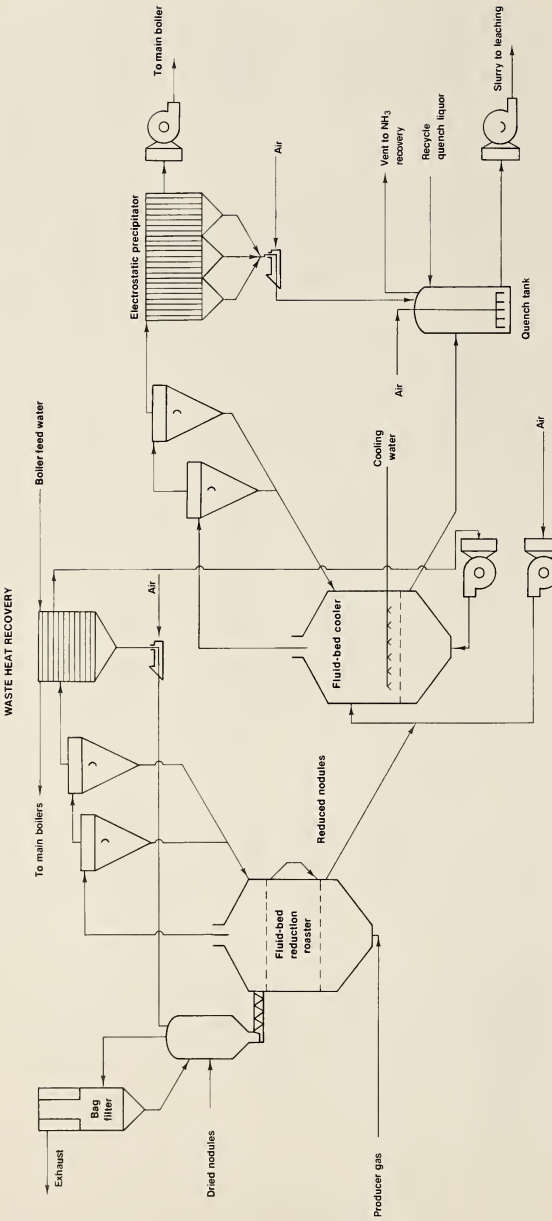


Figure A-3.—Reduction.

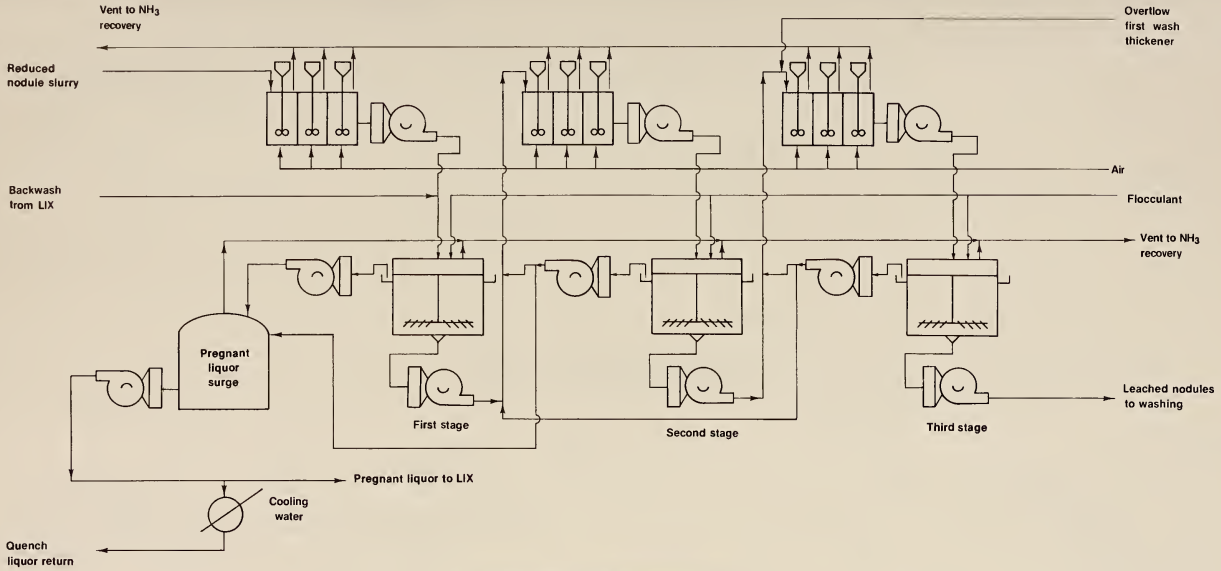


Figure A-4.—Leaching-aeration.

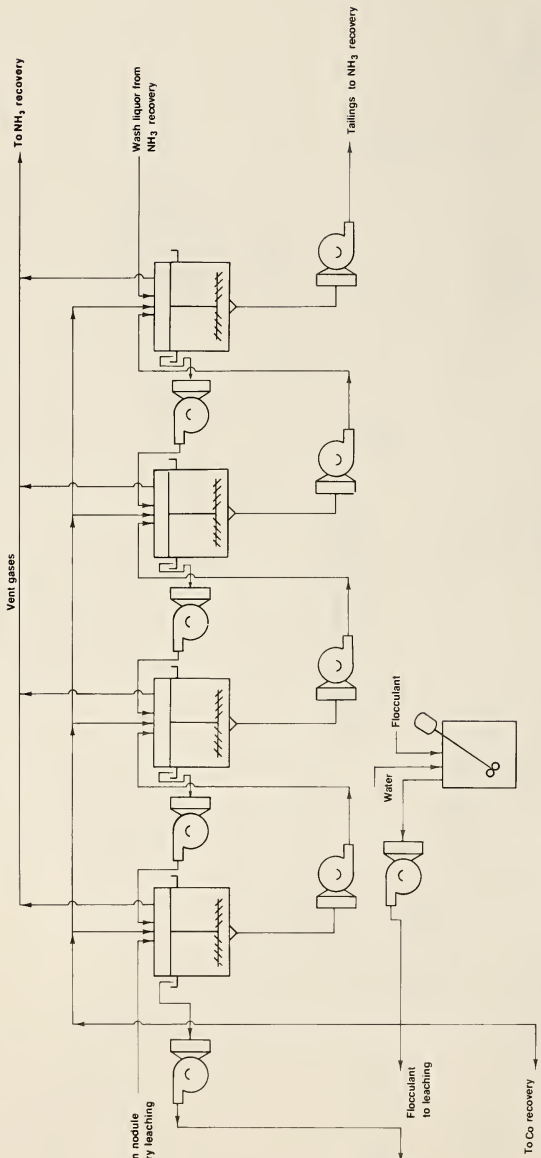


Figure A-5.—Solid-liquid separation.

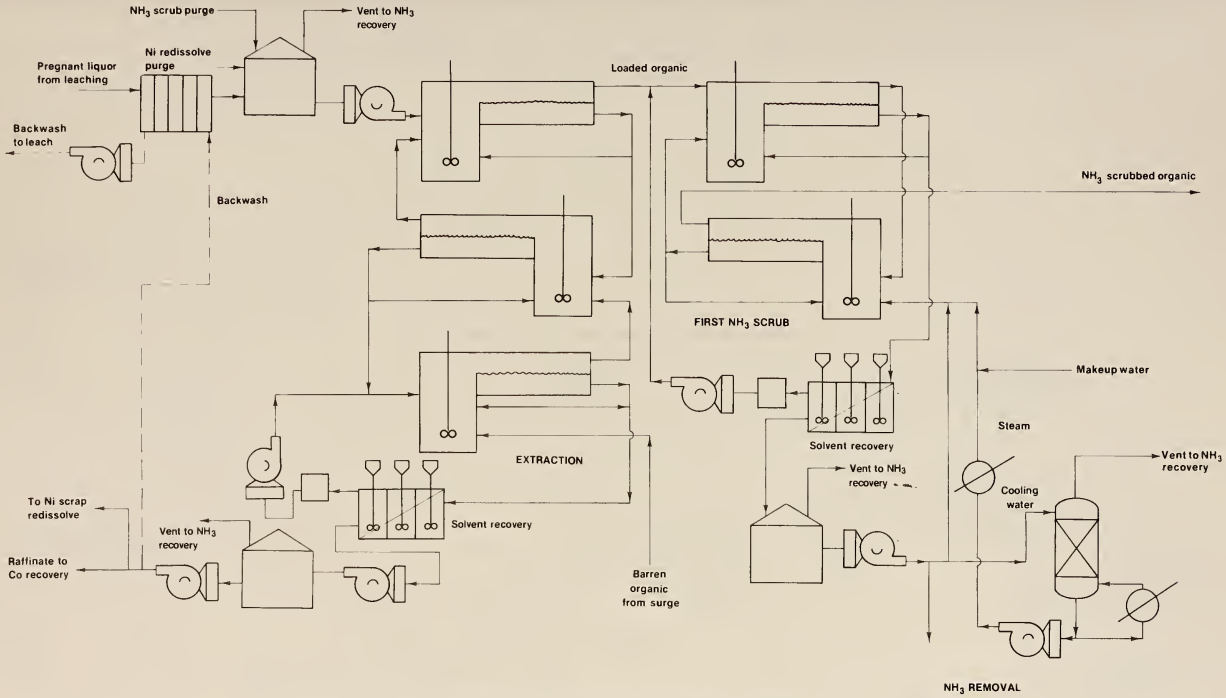


Figure A-6.—Liquid ion exchange-extraction.

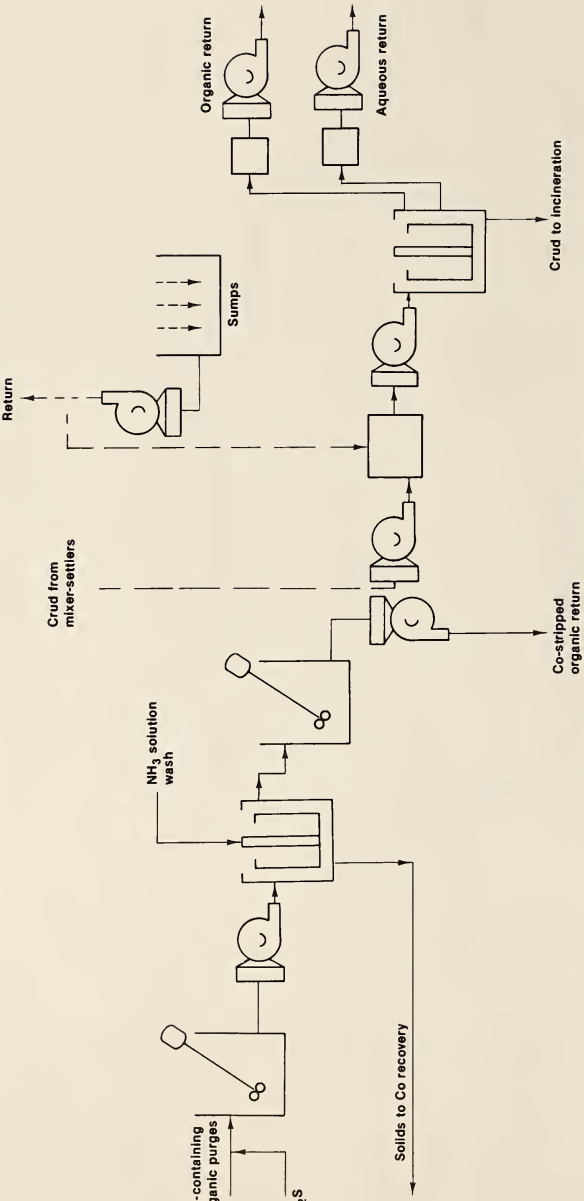


Figure A-7.—Cobalt stripping-organic purge.

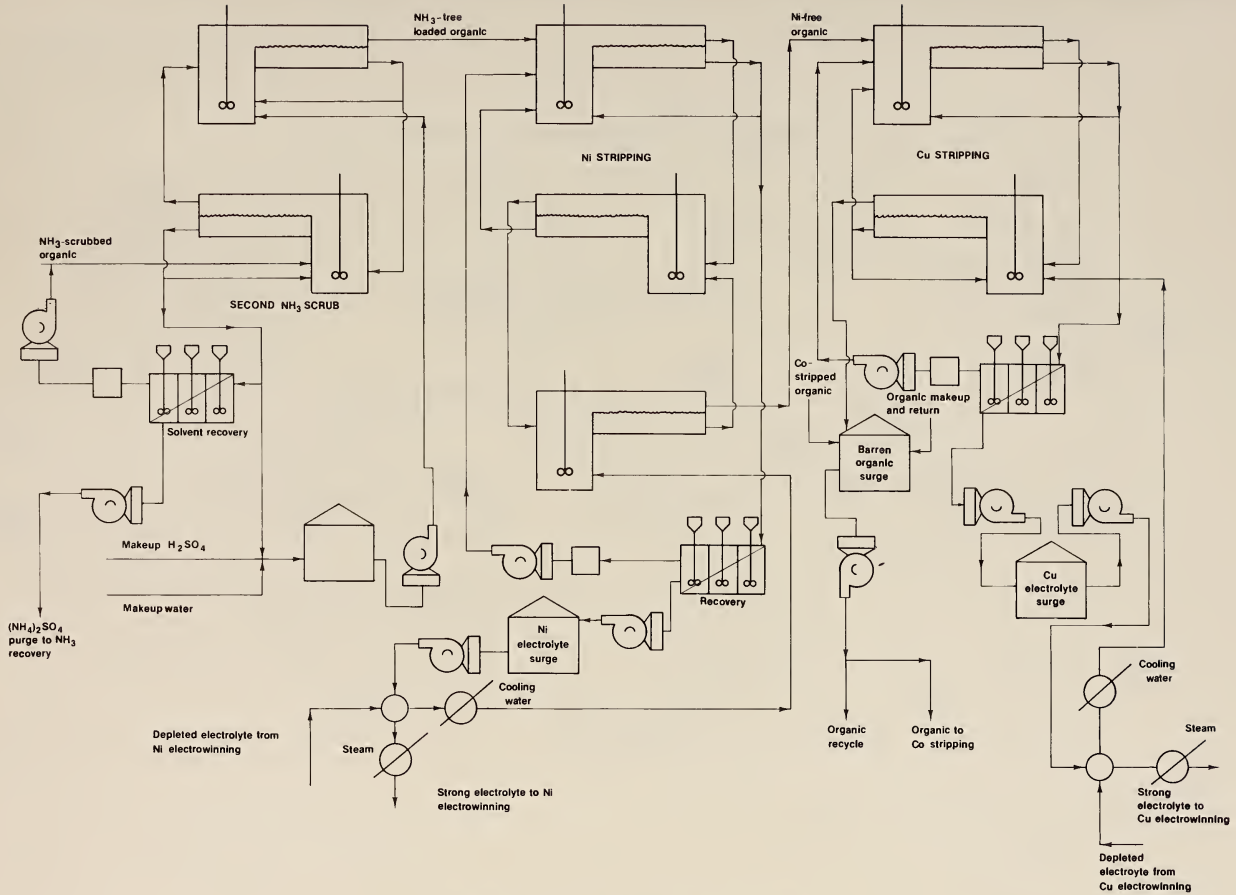


Figure A-8.—Liquid ion exchange-stripping.

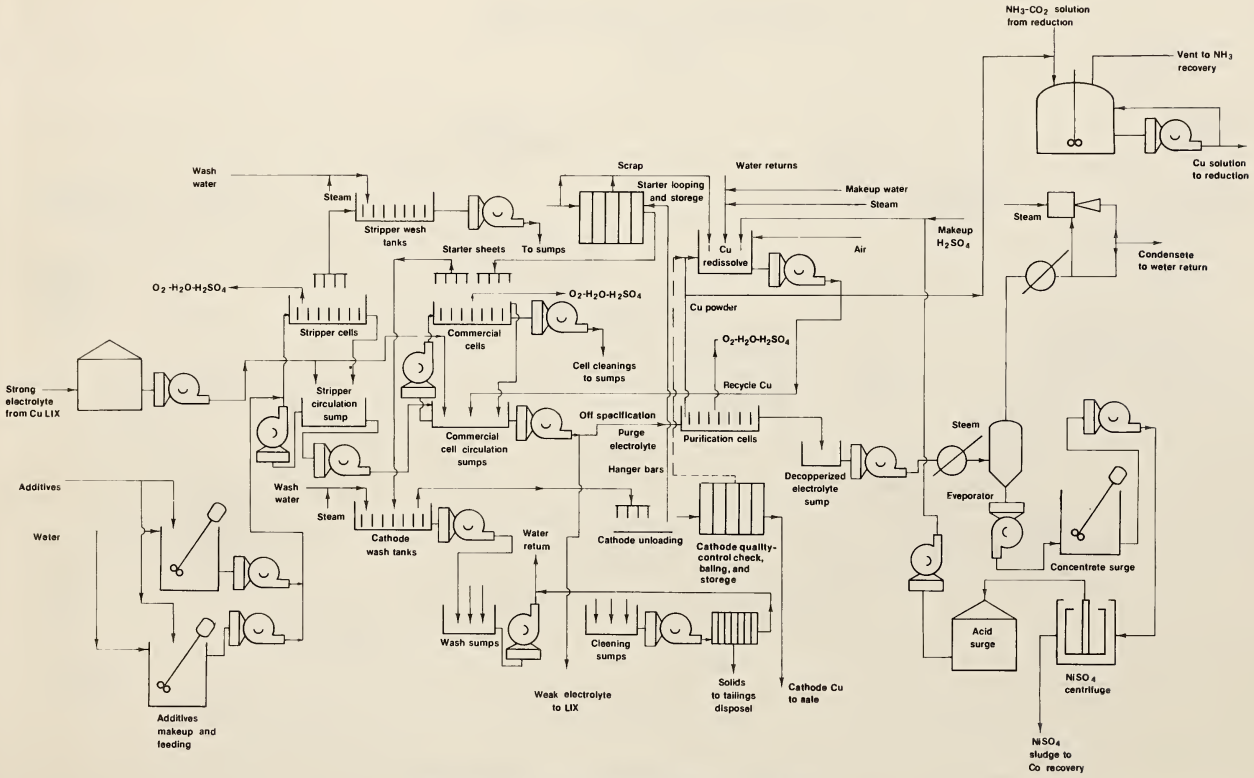


Figure A-9.—Copper electrowinning—commercial.

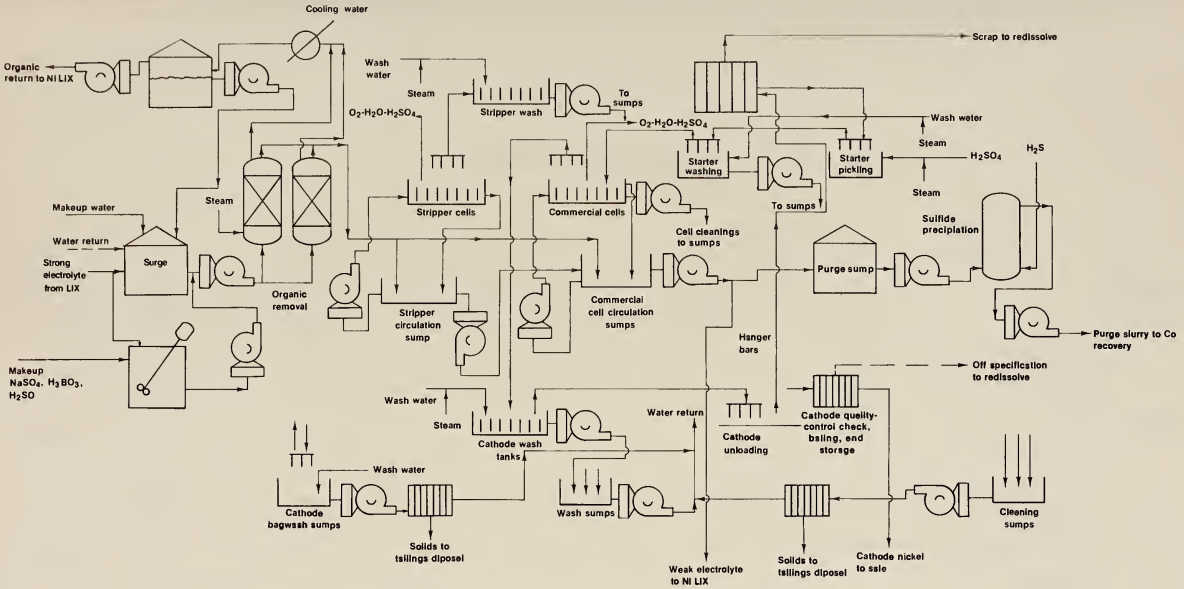


Figure A-10.—Nickel electrowinning—commercial.

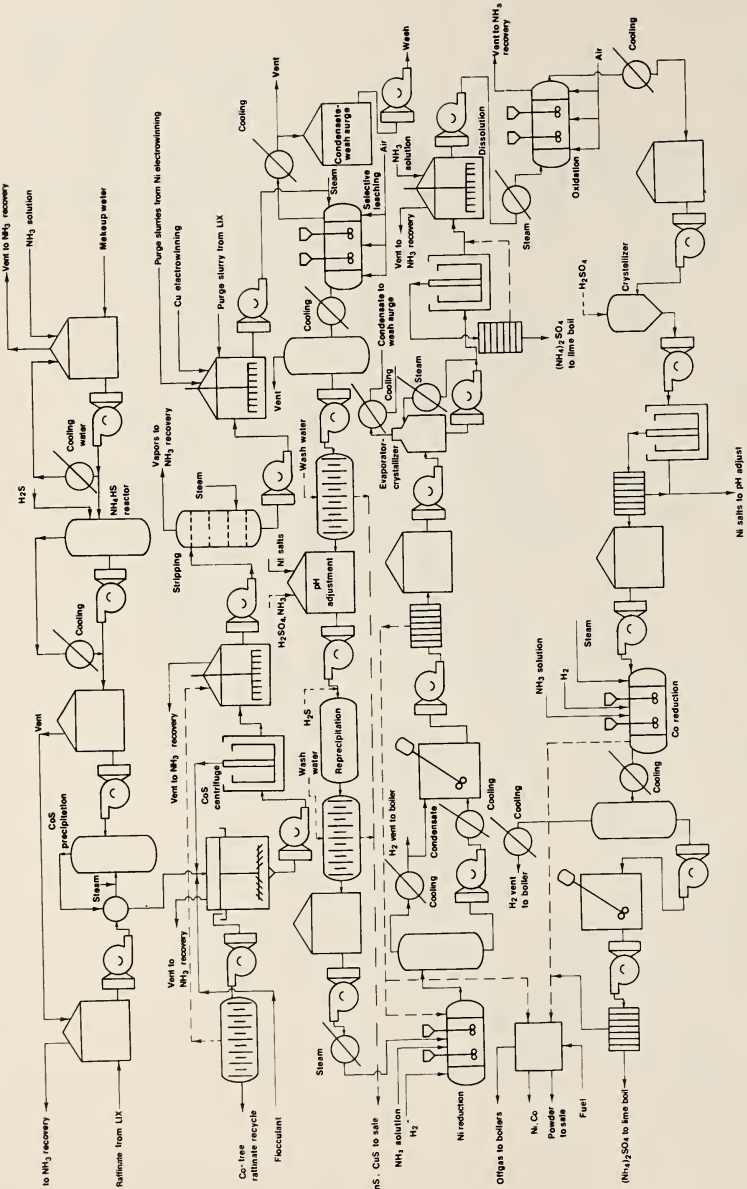


Figure A-11.—Cobalt recovery.

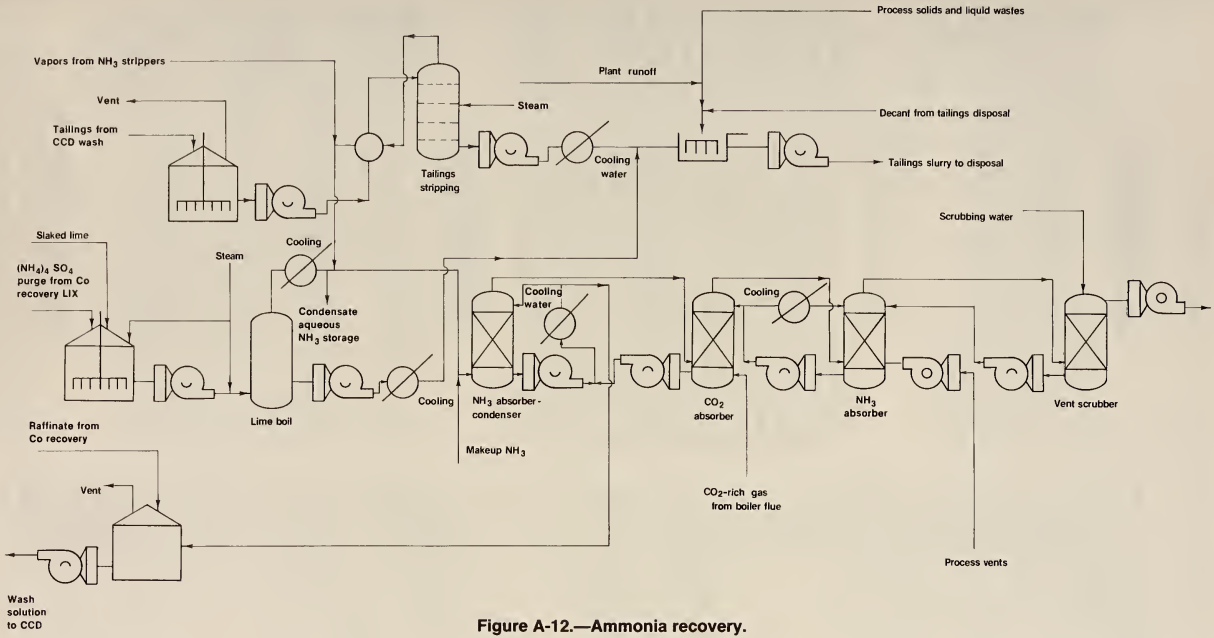


Figure A-12.—Ammonia recovery.

APPENDIX B.—CUPRION AMMONIACAL LEACH PROCESS

The Cuprion ammoniacal leach process is a three-metal process in which Cu, Ni, and Co are liberated in an ammoniacal-ammonium carbonate leach following a reduction-leach step. Carbon monoxide is used to regenerate the cuprous ion which reduces manganese dioxide. Copper and nickel are co-extracted by liquid ion exchange (LIX) reagents and are selectively stripped and recovered as electrowon cathodes. Cobalt is removed from the raffinate by precipitation with hydrogen sulfide and is recovered from the sulfide precipitate, along with some Ni, Zn, and Cu, by selective leaching and hydrogen reduction. The metal-free raffinate is steam stripped to recover a high-strength ammonia solution for recycle to the tailings wash step, together with ammonia and ammonium carbonate recovered by steam stripping the leach tailings.

Detailed descriptions of each segment of the process are given for the following flowsheets. A summary of parameters for each section is given in table B-1. A key to the flowsheet symbols is given in figure B-1.

ORE PREPARATION (FIG. B-2)

Wet nodules are reclaimed from storage and fed through a primary cage mill where they are reduced to minus ⅞ in. They then pass to a rod mill for wet grinding to minus 65 mesh. Oversized nodules are separated and returned via the rake classifier, hydrocyclone, water-recycle circuit. The ground nodule slurry passing through the cyclone is held in an air-agitated surge tank to prevent settling before being pumped to the reduction step.

REDUCTION-LEACH (FIG. B-3)

The nodule slurry is mixed with recycled strong ammonia solution and fed, with a recycled solution containing an excess of cuprous ion (Cu^+), to a train of agitated reduction reactors. The dilute slurry is contacted with a carbon monoxide-rich gas derived from gasified coal, the manganese dioxide is reduced and converted to manganese carbonate, and most of the value metals are solubilized. The heat of reaction is removed in shell and tube exchangers to maintain the reduction temperature at 50° C, and excess gases pass to ammonia recovery. The reduced, dilute nodule slurry is thickened with the overflow recycle, and the thickened pulp passes to the oxidation leach.

OXIDATION-LEACH (FIG. B-4)

The reduced nodule slurry passes to a countercurrent oxidizing leach in which air is sparged into the leach slurry to oxidize residual Cu^+ to Cu^{2+}, Co^{2+} to Co^{3+}, and Fe^{2+} to Fe^{3+}, precipitating the Fe as an insoluble ferric hydroxide in the manganese carbonate tailings. Liquid-solid separations are made in thickeners, which also provide residence time for leaching. Offgases from aeration pass to ammonia recovery, leached nodules to washing, and pregnant liquor to LIX for metal separation and purification.

SOLID-LIQUID SEPARATION (FIG. B-5)

Metal values that have been solubilized in leaching and absorbed on tailings are recovered from the tailings by washing in a countercurrent decantation (CCD) circuit using covered thickeners. Wash liquor consists of recovered ammonia and ammonium carbonate along with raffinate from cobalt recovery. Washed tailings pass to stripping for ammonia and ammonium carbonate recovery while the wash overflow passes to leaching.

LIQUID ION EXCHANGE-EXTRACTION (FIG. B-6)

Pregnant liquor from leaching is filtered and passes to a three-stage, countercurrent LIX extraction circuit where copper, nickel, and some ammonia are removed from the pregnant liquor. Most of the ammonia is removed from the organic phase by washing with a weak aqueous ammonia solution. This ammonia is recovered by steam stripping a portion of the scrub solution, with the vapors passing to the ammonia recovery section. Provision is made for periodically cleaning the mixer-settler units used in extraction and stripping and for recovering organic and aqueous phases for recycle. Degraded organic, dust, and other forms of "crud" are removed from the organic and incinerated. Because a small amount of Co is co-extracted and is not stripped with Cu and Ni, it must be removed from the LIX reagent to prevent its buildup. This is accomplished by precipitating the cobalt, with hydrogen sulfide, from a purge stream of organic. The precipitated solids are washed from the organic and pass to cobalt recovery, while the purified organic is returned to the extraction loop (fig. B-7).

LIQUID ION EXCHANGE-STRIPPING (FIG. B-8)

The remainder of the ammonia is removed from the loaded organic by washing with a slightly acidic ammonium sulfate solution. The ammonium sulfate formed in scrubbing is purged to ammonia recovery. Nickel is then selectively stripped from the organic by countercurrent contact at controlled pH with depleted electrolyte from nickel electrowinning. Because electrowinning conventionally occurs at a higher temperature than operation of the LIX circuit, the strip solution is heated passing to electrowinning and cooled passing from electrowinning. Copper is then removed from the nickel-free organic by countercurrent stripping with depleted electrolyte from copper electrowinning. The copper electrolyte is also heated-cooled on passage to-from electrowinning to permit operation of electrowinning at a higher temperature. Makeup organic is added to the stripped reagent to offset degradation and soluble organic losses to the pregnant liquor, and the metal-free organic is recycled to extraction.

COPPER ELECTROWINNING—COMMERCIAL (FIG. B-9)

Cathode copper is recovered from the LIX strong electrolyte using conventional technology. Starter sheets are deposited

Table B-1.—Operating parameters for Cuprion ammoniacal leach process

Parameter and unit	Value
ORE PREPARATION (FIG. B-2)	
Feed rate, wet basis (330 days/yr; 24 hr/day)	10,900
Feed size to reduction, mesh	−65
Pulp density, solids	35
REDUCTION-LEACH (FIG. B-3)	
Reductant gas composition, pct:	
CO	40-60
H_2	30-45
H_2O	6-12
N_2	1
Temperature, °C	50
Pressure, atm	1
Reduction reactions:	
$MnO_2 + CO \rightarrow Mn\,CO_3$	
$Fe_2O_3 + CO \rightarrow 2FeO + CO_2$	
$NiO + CO \rightarrow Ni + CO_2$	
$CuO + CO \rightarrow Cu + CO_2$	
$CoO + CO \rightarrow Co + CO_2$	
Leachate composition, gpl:	
NH_3	100
CO_2	25
Cu	3-5
Number of stages	6
Reduction, pct:	
Co	50
Cu	80
Mn	97
Mo	80
Ni	90
Zn	40
Slurry density, pct solids	20-30
OXIDATION-LEACH (FIG. B-4)	
Pregnant liquor composition, gpl:	
NH_3	100
CO_2	25
Cu	4-8
Ni	5-10
Temperature, °C	50
Pressure, atm	1
Recovery, pct:	
Co	50
Cu	90
Ni	90
SOLID-LIQUID SEPARATION (FIG. B-5)	
Underflow density, pct solids	35-40
Wash ratio, kg/kg liquor	2
Wash recovery, pct	98
Number of stages	6
Wash liquor composition, gpl:	
NH_3	100
CO_2	50
LIQUID ION EXCHANGE-EXTRACTION (FIG. B-6)	
Extraction:	
Extractant	[1]LIX 64N
Number of stages	3
Organic-aqueous ratio	2:1
Metals extraction, pct:	
Co	1
Cu	99.9
Ni	99.9
Zn	10
Washing (primary):	
Washing agent, pct NH_3	1
Number of stages	2
Organic-aqueous ratio	3:1
Residual NH_3 in organic, gpl	0.1

Parameter and unit	Value
LIQUID ION EXCHANGE-STRIPPING (FIG. B-8)	
Washing (secondary):	
Wash composition, gpl:	
$(NH_4)_2SO_4$	200
H_2SO_4	1
Number of stages	2
Organic-aqueous ratio	1:1
Residual NH_3 in organic, gpl	0.01
Ni stripping:	
Strip solution composition, gpl:	
Cu	<0.001
H_2SO_4	40.
Ni	50
Zn	≈0
Number of stages	3
Organic-aqueous ratio	5:1
Stripping, pct:	
Co	0.3
Cu	<.004
Ni	98.8
Zn	≈0
Cu stripping:	
Strip solution composition, gpl:	
Cu	40
H_2SO_4	160
Ni (max)	10
Zn	5
Number of stages	2
Organic-aqueous ratio	3:1
Stripping, pct:	
Co	0.2
Cu	87
Ni	≈0
Zn	100
Temperature, °C	40
COPPER ELECTROWINNING—COMMERCIAL (FIG. B-9)	
Current density, A/m^2	180
Current efficiency, pct	94
Temperature, °C	50
Cu in-out, gpl	53-40
H_2SO_4 in-out, gpl	160-180
NICKEL ELECTROWINNING—COMMERCIAL (FIG. B-10)	
Current density, A/m^2	180
Current efficiency, pct	93
Temperature, °C	60
Ni in-out, gpl	75-50
H_2SO_4 in-out, gpl	0.016-40
Na_2SO_4, gpl	100
H_3BO_3, gpl	15
COBALT RECOVERY (FIG. B-11)	
Precipitating agent, pct NH_4HS	30
Precipitation, pct:	
Co	98
Cu	99.9
Ni	99
Zn	99.9
Temperature, °C	80
Clarifier density, pct solids	5
Wash ratio	2:1
Co leaching: slurry, pct	40
Leaching agent, pct H_2SO_4	70
Evaporation-crystallization water removal, pct	70
Co oxidation:	
Temperature, °C	100
Pressure, psig	150
Co reduction:	
Temperature, °C	175
Pressure, psig	500
Reductant	H_2

[1]Reference to specific tradenames does not imply endorsement by the Bureau of Mines.

Table B-1.—Operating parameters for Cuprion ammoniacal leach process—Continued

Parameter and unit	Value
AMMONIA RECOVERY (FIG. B-12)	
CO_2 absorber:	
Temperature ..... ° C..	40
Pressure ..... atm..	1.2
Efficiency for CO_2 ..... pct..	99
Number of stages	1
NH_3 absorber:	
Temperature ..... ° C..	35
NH_3 absorber—Con.	
Pressure ..... atm..	1.2
Number of stages	1
NH_3 stripper:	
Pressure ..... atm..	1.5
Recovery of NH_3 ..... pct..	99
Number of stages	2

on titanium blanks from strong electrolyte and are removed, washed, looped, and returned to the commercial section as starters. Full-term cathodes produced in the commercial section are washed, unloaded, and prepared for shipment to sale. The greater portion of the weak electrolyte is recycled to the LIX section for stripping. A small amount of nickel is stripped along with the copper not deposited in electrowinning, and must be purged from the system. The purged electrolyte passes through purification cells where copper is removed by electrowinning to depletion. The decopperized electrolyte passes to vacuum evaporators where water is removed and nickel sulfate is precipitated from the resulting highly acidic solution. The nickel sulfate is removed and sent to cobalt recovery where it is combined with other purge streams. The acid is returned to the process where, with makeup acid, it is used to redissolve scrap copper for return to the commercial cells for deposition. Provisions are made for recycling copper, in ammonium carbonate solution, to reduction if required. Sufficient steam, wash water, and makeup water are added to the circuit to offset water vaporized or carried off with evolved oxygen during electrowinning.

NICKEL ELECTROWINNING—COMMERCIAL (FIG. B-10)

Nickel is recovered from the strong electrolyte by electrowinning in a manner similar to that used for copper recovery. In nickel electrowinning, however, cathode bags are used, and sodium sulfate and boric acid are added to the electrolyte to control its conductivity and pH. Dissolved organic carried from the LIX step is removed by adsorption on activitated carbon before the nickel electrolyte passes to electrowinning. Also, the starter sheets are pickled in H_2SO_4 prior to use in the commercial cells, and nickel scrap is redissolved in ammonia-containing raffinate and recycled to the pregnant liquor, rather than to the recycled or makeup acid solution. The electrolyte purge required to remove impurities from the electrowinning circuit passes to a sulfide precipitation reactor and then to cobalt recovery for recovery of metal values.

COBALT RECOVERY (FIG. B-11)

Along with unextracted Cu, Ni, and Zn, Co is recovered from the LIX raffinate by precipitation with a slight excess of ammonium hydrosulfide (produced by sparging hydrogen sulfide into an excess of ammonia solution). The sulfide precipitate is separated from the raffinate in a clarifier, with the clarifier overflow being recycled to ammonia recovery and the underflow passing to stripping for ammonia recovery.

The sulfide slurry is mixed with electrolyte purges from Cu and Ni electrowinning, and with the Co recovered from stripping the LIX reagent. The mixture is pressure-leached with air to preferentially dissolve the Ni and Co sulfides, leaving the Cu and Zn sulfides in the residues. The latter are removed by filtration and sold as minor products to smelters for recovery of metal values.

Following pH adjustment and reprecipitation with hydrogen sulfide for final removal of any Zn and Cu solubilized in the first leach, the Ni-Co sulfate solution is heated and autoclaved, and Ni is reduced with hydrogen. Sufficient ammonia solution is added during reduction to neutralize the acid formed. Only a portion of the nickel is removed per pass to prevent overreduction and subsequent contamination of the nickel powder with cobalt. After densification through repeated recycle, the nickel powder is removed, washed, and passed to drying and briquetting for sale.

The largely nickel-free cobalt sulfate solution passes to an evaporator-crystallizer where the remaining nickel and cobalt are precipitated as the double salts with ammonium sulfate. Excess ammonium sulfate is purged, and the salts are redissolved in strong ammonia solution. The cobalt in solution is oxidized to the cobaltic state (Co^{3+}) with air. This permits the cobalt to remain in solution when the stream is acidified to remove the nickel salts, which are separated and recycled to the pH adjustment step. The nickel-free solution is then heated and autoclaved for removal of cobalt by hydrogen reduction. Sufficient ammonia is added to neutralize the acid generated. The cobalt powder is dried and briquetted for sale, while the ammonium sulfate is purged to the ammonia recovery process.

AMMONIA RECOVERY (FIG. B-12)

Tailings from the CCD wash circuit are preheated and stripped for ammonia and carbon dioxide recovery by countercurrent contact with steam in stripping towers. The steam and ammonia-carbon dioxide vapors from tailings stripping are combined with vapors from cobalt sulfide slurry stripping, condensed, and combined with ammonia and carbon dioxide scrubbed from process vent streams. Makeup carbon dioxide is obtained from boiler offgases by countercurrent contact with scrubbing water; the ammonia-free gases pass to stacks for disposal. The ammonia-rich ammonium carbonate solution required in reduction is obtained by stripping only a portion of the ammonia contained in the raffinate stream from cobalt recovery. These ammonia-rich vapors are combined with ammonium-steam vapors from the LIX ammonia recovery and lime boil steps, makeup ammonia, and ammonia-rich vapors from reduction and oxidation vents, and are condensed and recycled to reduction. The raffinate is then stripped further, with the ammo-

nium carbonate recycled to tailings washing and the stripper bottoms used for process water makeup.

Ammonia is recovered from the ammonium sulfate purges from cobalt recovery and the LIX washing step by reaction with slaked lime. Steam is blown into the mixture to strip the evolved ammonia, and the vapor is condensed, with the condensate returned for recycle within the process. The gypsum slurry from the lime boil is cooled, along with the slurry from the tailings stripping, and passed to tailings surge. This is combined with the process solid and liquid wastes and plant runoff, treated for pH control as required, and pumped to the tailings impoundment area for disposal.

PLANT SERVICES

Plant services include process and cooling water supply and treatment, steam raising and power generation, gas treatment, and reducing gas preparation. Makeup water is clarified and softened for distribution to the process as required. Additional treatment is required for cooling tower water makeup, boiler feed water makeup, and for supplying plant potable water. The carbon monoxide required for manganese reduction is produced in a low-pressure gasifier in which coal is mixed with oxygen and steam and partially combusted. Acid gases are removed from the reducing gas, following particulate removal, and are sent to the main boilers to oxidize reduced components for subsequent recovery. High-strength carbon monoxide is then removed from the sweetened gases for use in reduction, and the remaining gases, mainly hydrogen, are sent to the main boilers except for the amount required in cobalt reduction.

These and other combustible process offgases are burned, along with additional coal, in the main boilers to raise the required process steam and to generate a portion of the power required in the process. Following particulate removal, the flue gases are combined with other process offgases and pass to gas treatment, where sulfur oxides and other constituents are removed by scrubbing with limestone. The scrubbed offgases are reheated, combined with scrubbed vents from ammonia recovery, and are passed to stacks for disposal.

MANGANESE PRODUCTION ADD-ON

The recovery of manganese from ammoniacal leach tails is an option that has been investigated. Manganese may be partially recovered from tailings by flotation of the fine $MnCO_3$ present. The $MnCO_3$ could then be converted to an oxide form for feed to produce ferromanganese or other manganese alloys. The recovery of manganese from the process tails would be contingent on the market conditions and process economics. Some intermediary product may have market value, thereby avoiding energy-intensive steps to produce manganese alloys. Because of the relatively new technology required for manganese recovery from ammoniacal leach tails, and the dependency upon economic and technical conditions, no detailed flowsheets are presented for this process.

PROCESS ALTERNATIVES

A major process alternative, involving the pyrometallurgical reduction-ammoniacal leaching of nodules, is fully documented in appendix A.

While the pyrometallurgical reduction-ammoniacal leaching process is closely based on the well-known Caron process, the Cuprion process differs in two important respects: the metals separation scheme is specific to nodules processing and the differing ammonium carbonate concentrations required in reduction and tailings washing complicate the ammonia recovery step.

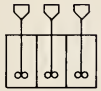
Alternative configurations of the metals separation steps are possible, such as selective extraction-selective stripping, but their impact on overall plant material and energy balances should be minor. Many variations are possible in the details of the scheme used for recovery of cobalt from a mixed sulfide precipitate. Ultimately, however, their impact on plant requirements would not differ greatly from the approach used here, because the sulfides will still be oxidized to sulfates, purged, and hydrogen reduced. It does not appear likely that solutions could be purified easily enough to permit recovery of electrolytic cobalt.

Tailings stripping for ammonia and carbon dioxide recovery has been based on the Caron practice, but the raffinate stripping operation is unique to this process. No operating data are available to support the energy-intensive concept used. It is possible that other techniques, such as vacuum or pressure stripping, pH adjustment prior to stripping, extractive distillation, etc., may be more advantageous if other process constraints, such as the overall water balance, can also be met.

The ammonium sulfate solutions purged from the liquid ion exchange-extraction and cobalt recovery sections have been treated with lime for the recovery of ammonia for recycle. An alternative approach would involve direct recovery of ammonium sulfate by evaporation-crystallization, for sale as a byproduct.

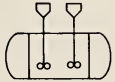
It has been assumed that, except for the cobalt reduction requirements, byproduct hydrogen from carbon monoxide production would be burned for its fuel value, which is a relatively poor use. A small part (1 pct) of the hydrogen could be burned with 4,000-tpy sulfur to produce the required amount of hydrogen sulfide.

Absorber



Aerator

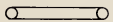
Agitator



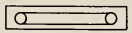
Autoclave

Blower

Centrifuge



Conveyor



Covered conveyor

Cyclone

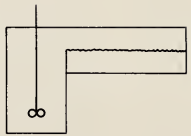
Ejector

Filter

Filter

Heat exchanger

Hopper

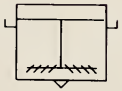


Mixer-settler

Pump

Surge tank

Surge tank, agitated



Thickener

Figure B-1.—Key to symbols.

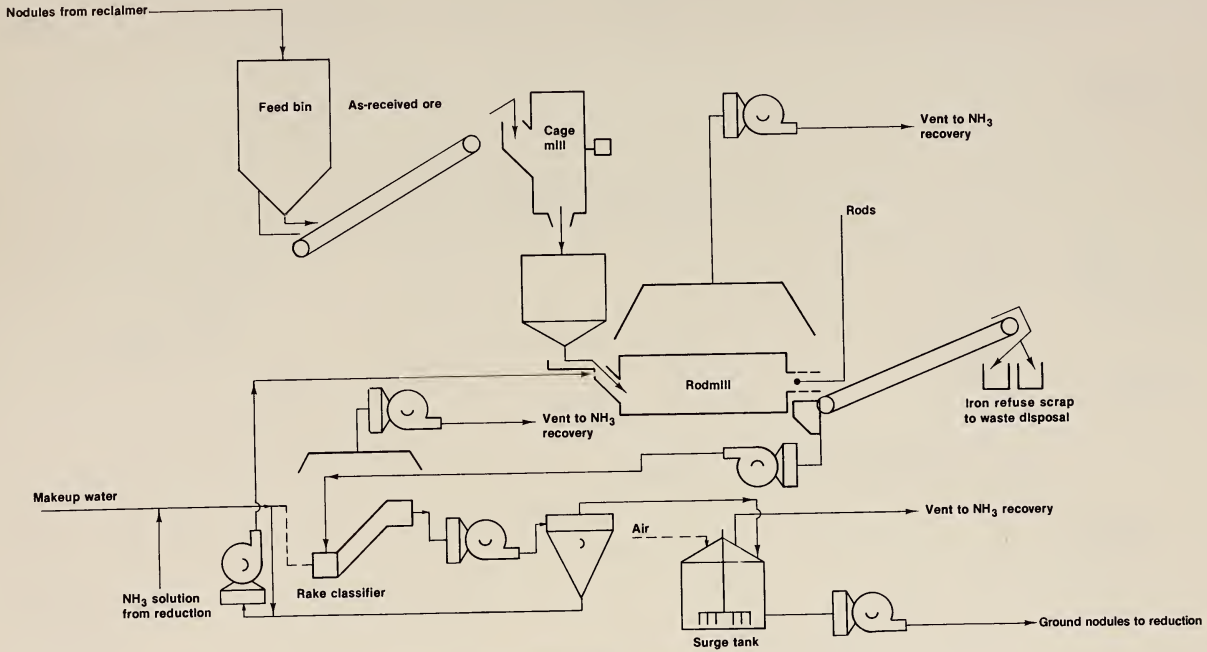


Figure B-2.—Ore preparation.

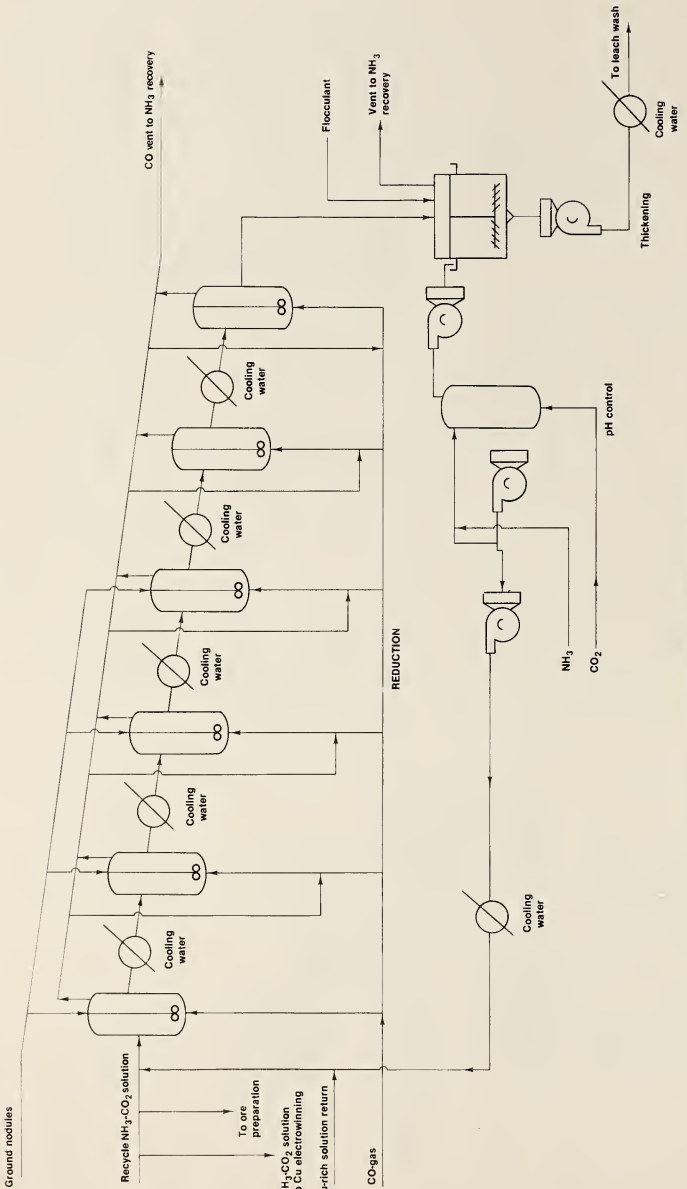


Figure B-3.—Reduction-leach.

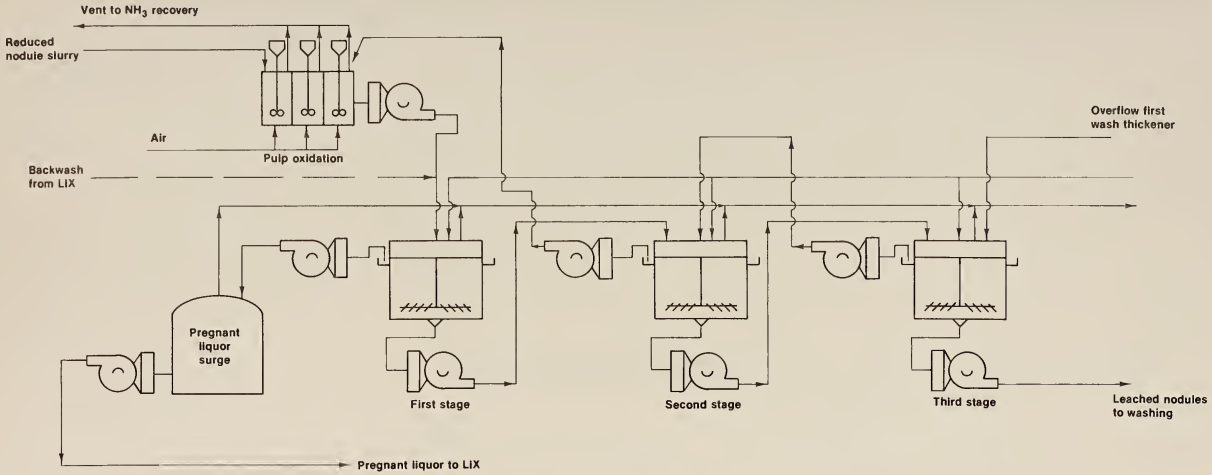


Figure B-4.—Oxidation-leach.

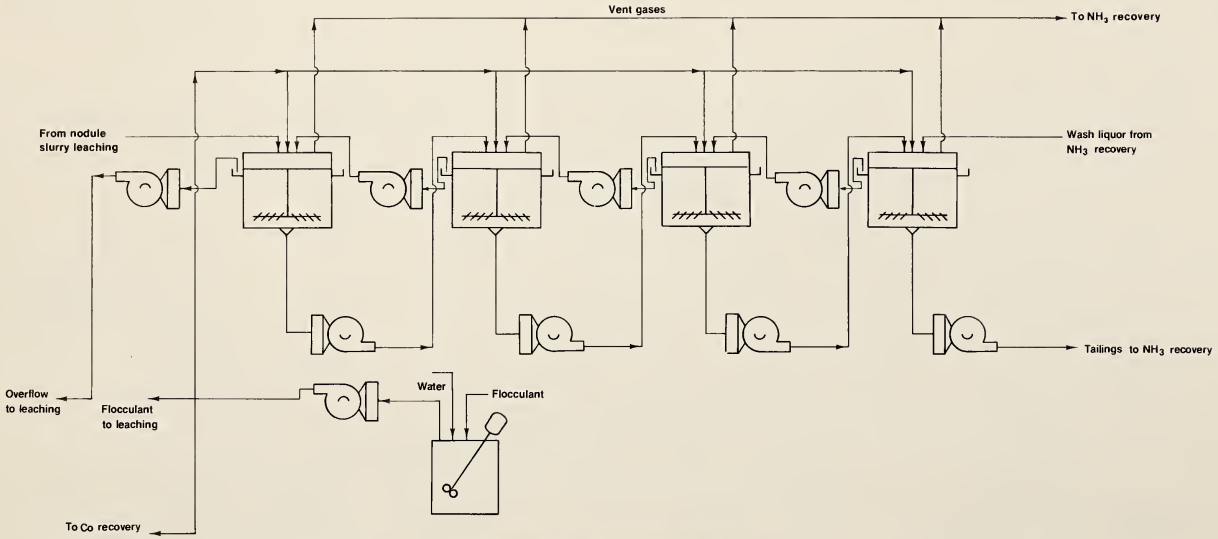


Figure B-5.—Solid-liquid separation.

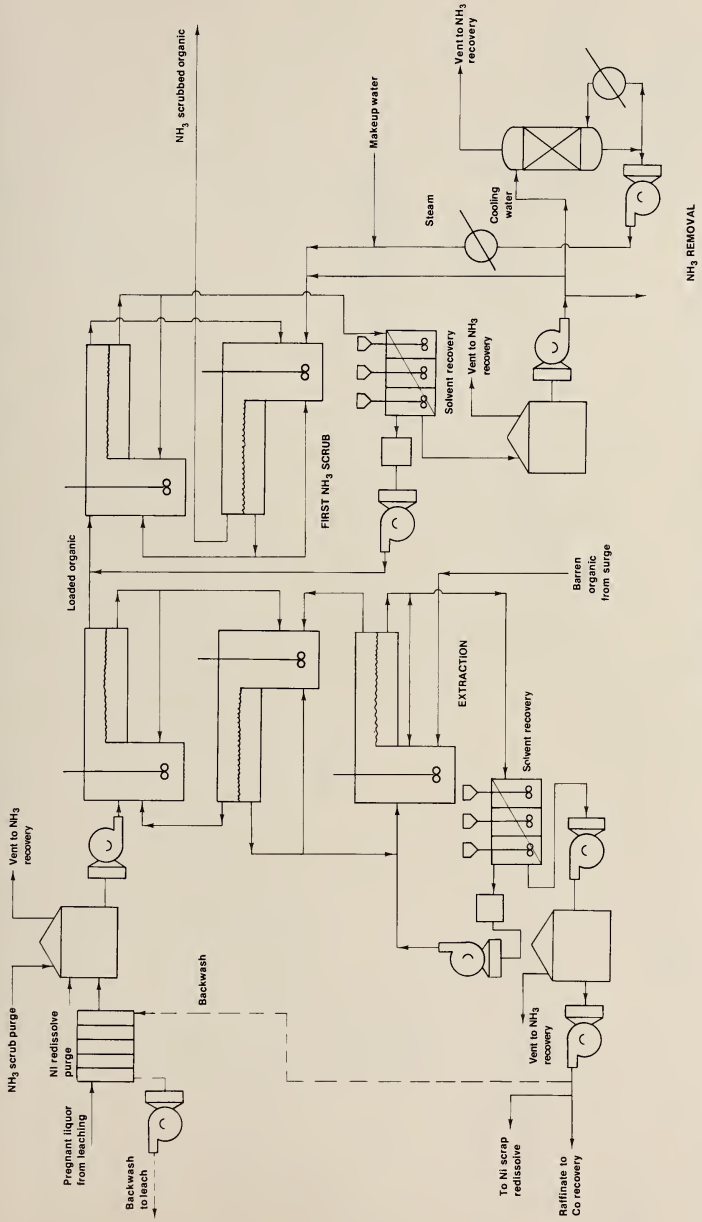


Figure B-6.—Liquid ion exchange-extraction.

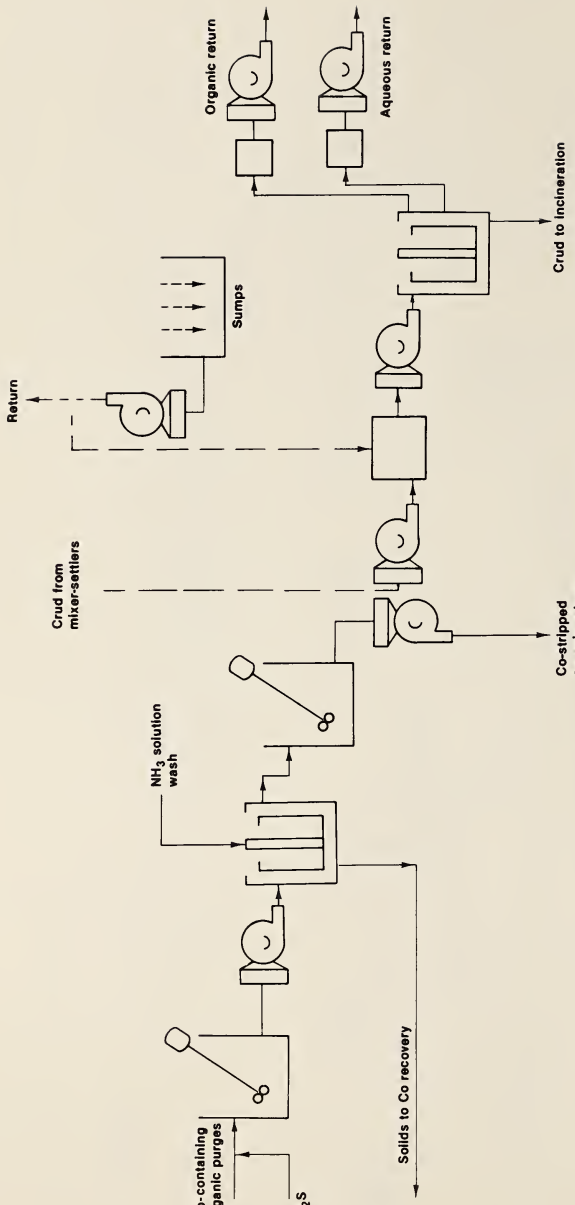


Figure B-7.—Cobalt stripping-organic purge.

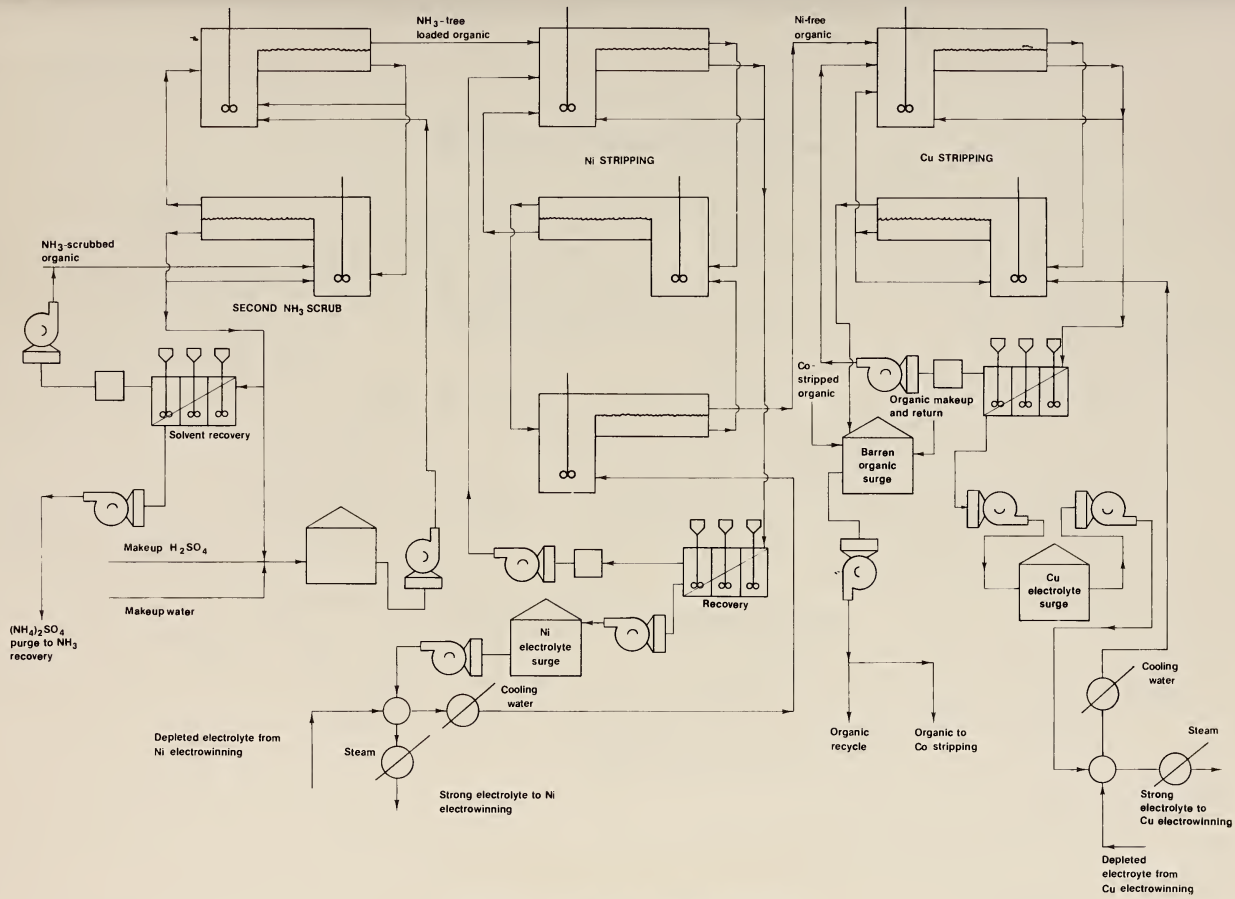


Figure B-8.—Liquid ion exchange-stripping.

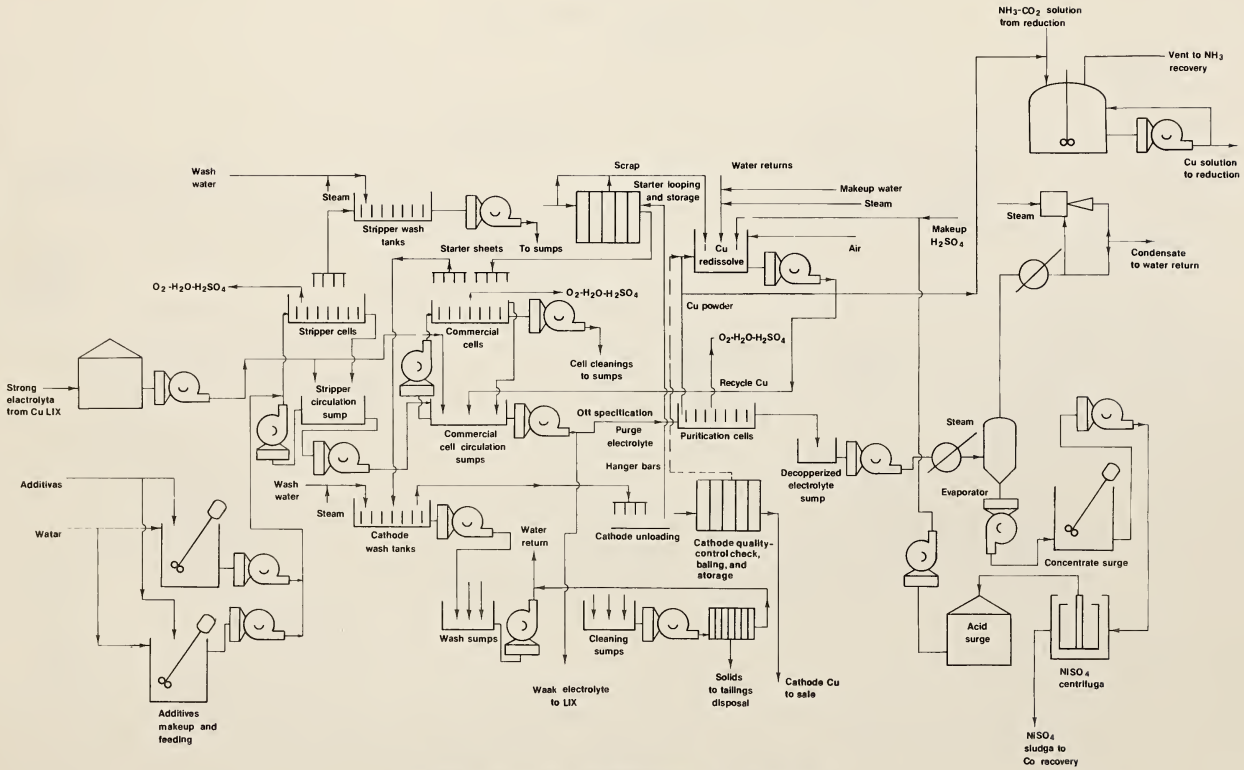


Figure B-9.—Copper electrowinning—commercial.

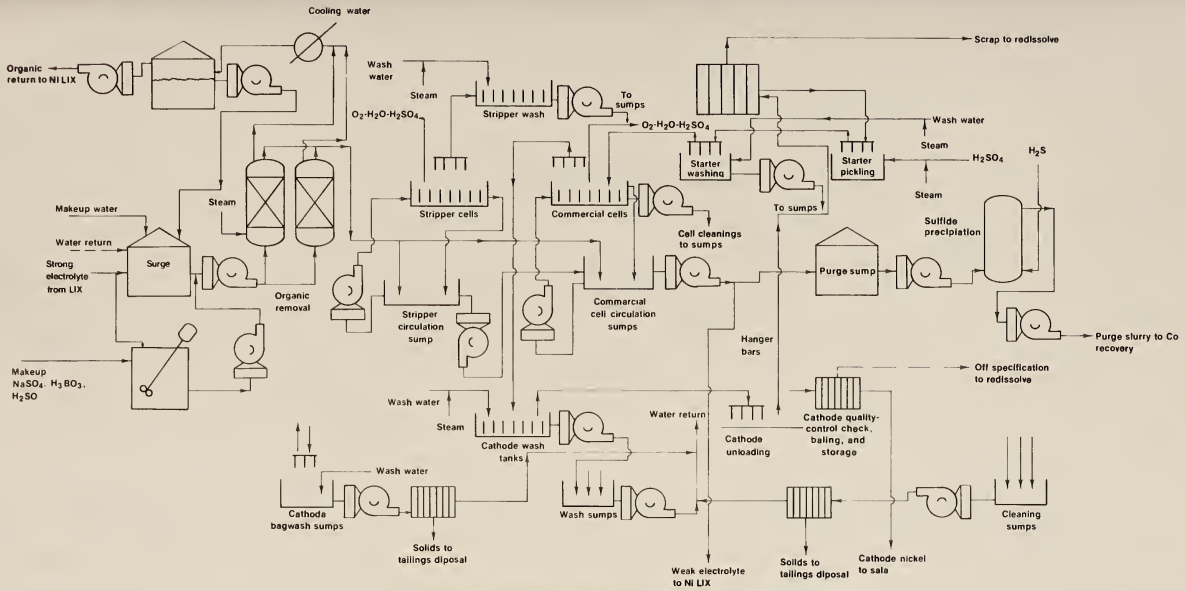


Figure B-10.—Nickel electrowinning—commercial.

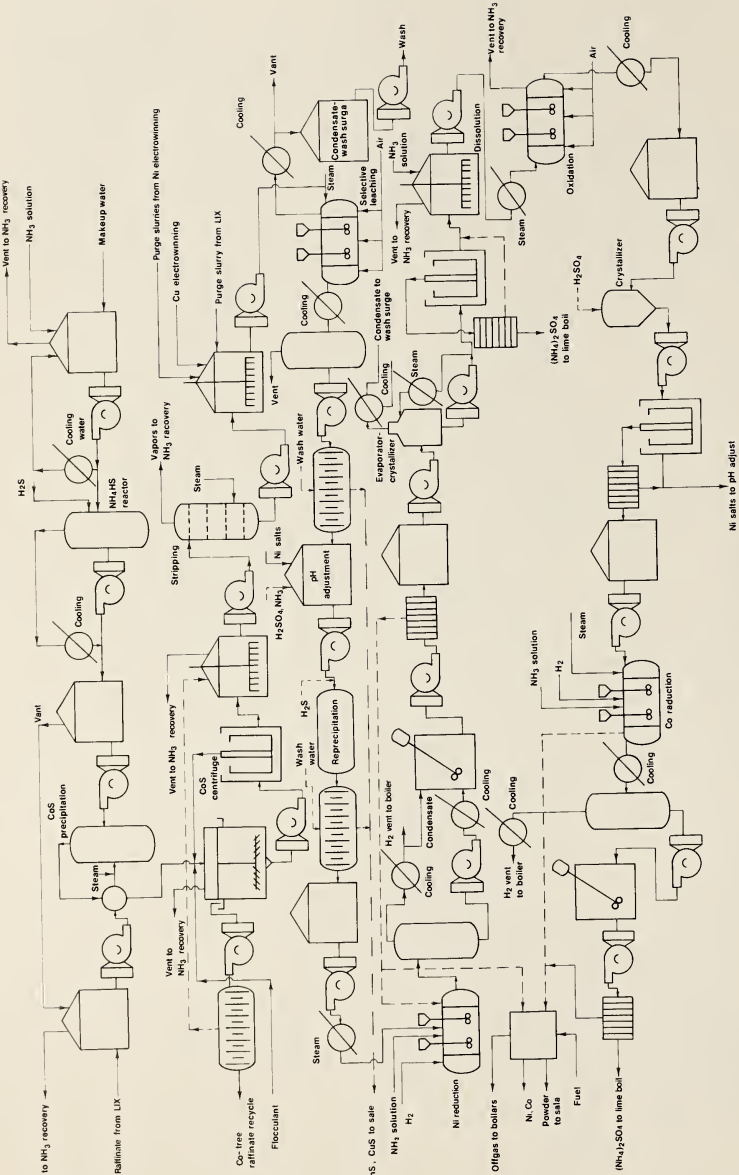


Figure B-11.—Cobalt recovery.

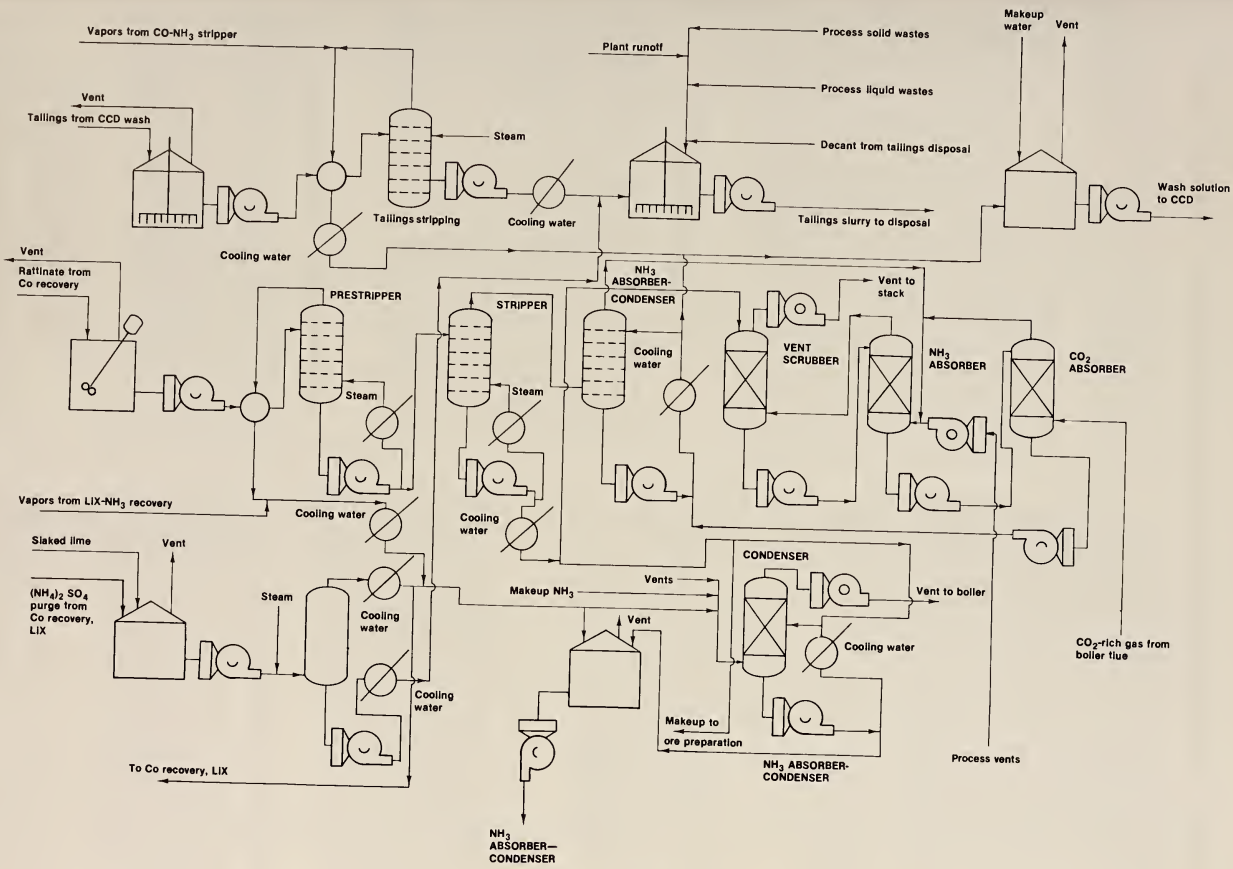


Figure B-12.—Ammonia recovery.

APPENDIX C.—HIGH-TEMPERATURE AND HIGH-PRESSURE H_2SO_4 LEACH PROCESS

The high-temperature and high-pressure H_2SO_4 leach process is a three-metal process in which Cu, Ni, and Co are selectively leached from the nodules by strong H_2SO_4 at high temperature and high pressure. After separation of the leaching residue and metalliferous solution by washing, the copper and nickel are co-extracted by liquid ion exchange (LIX) reagents and are selectively stripped and recovered as electrowon cathodes. Cobalt is separated from the raffinate by precipitation with hydrogen sulfide and is recovered from the sulfide precipitate, along with some Ni, Cu, and Zn, by selective leaching and hydrogen reduction. The metal-free raffinate is recycled to the washing process. Ammonia consumed in the process is recovered and recycled to the process for use in pH control.

Detailed descriptions of each segment of the process are given for the following flowsheets. A summary of operating parameters for each section is given in table C-1. A key to the flowsheet symbols is given in figure C-1.

ORE PROCESSING (FIG. C-2)

Wet nodules are reclaimed from storage and fed through a primary cage mill where they are reduced to minus ⅞ in. They then pass to a rod mill for a second and final size reduction to minus 65 mesh. Oversized nodules that escape the initial rod milling are separated and returned via a rake classifier, hydrocyclone, water-recycle circuit. The ground nodule slurry passing through the hydrocyclone is held in an air-agitated surge tank to prevent settling until it can be fed to the high-temperature H_2SO_4 leach reactors.

LEACHING (FIG. C-3)

Slurried nodules enter a steam-sparged preheater along with the pregnant liquor of recycled leach solution containing the metal values. The solution at 105° C passes through a second steam-operated heat exchange step, reaching 170° C by use of sparged steam. A final temperature of 245° C is reached within the leach reactors, where contact with H_2SO_4 is made. After a set residence time within the reactors, the slurry passes through two pressure and one vacuum flash stage for steam heat recovery and slurry temperature reduction to 50° C.

SOLID-LIQUID SEPARATION (FIG. C-4)

Metal values that have been solubilized in acid leaching are recovered from the tailings by washing in a countercurrent decantation (CCD) circuit using covered thickeners. Adequate residence time in this circuit allows recycled water to wash the solubilized metal values from the precipitated and unreacted solids that pass from the system to a waste disposal area. The pregnant liquor proceeds to an initial pH adjusting step in preparation for selective metal removal.

PREGNANT LIQUOR pH ADJUSTMENT (FIG. C-5)

The pH adjustment process removes the necessary residual acid concentration of the pregnant liquor through the use of calcium carbonate (limestone). The calcium sulfate precipitate is sent to the wash circuit, while the neutralized pregnant liquor overflow of the clarifier goes to the copper LIX circuit.

COPPER LIQUID ION EXCHANGE (FIG. C-6)

The filtered pregnant liquor passes to a three-stage countercurrent LIX circuit with interstage pH adjustment. Nearly complete removal of the Cu from the aqueous to the organic exchange liquid is accomplished along with the removal of small amounts of Ni, Co, and Zn. The loaded organic stream is countercurrently stripped of its copper value with depleted electrolyte from copper electrowinning. The copper electrolyte is heated on passage to electrowinning and cooled on passage from electrowinning to permit operation of electrowinning at a higher temperature. Makeup organic is added to the electrolyte-stripped reagent to offset degradation and soluble organic losses to pregnant liquor. A continuous purge is operated to prevent a buildup of impurities (fig. C-7). The aqueous raffinate stream containing the nickel, cobalt, and other metal values is sent to a neutralizing step prior to nickel recovery.

COPPER ELECTROWINNING—COMMERCIAL (FIG. C-8)

Cathode copper is recovered from the LIX strong electrolyte using conventional technology. Starter sheets are deposited on titanium blanks and are removed, washed, looped, and returned to the commercial section. Cathodes produced in the commercial section are washed, unloaded, and prepared for shipment to sale. The major portion of the weak electrolyte is recycled to the LIX section for stripping. A small purge stream is recycled to the pH adjustment process to prevent a buildup of undesirable co-stripped metals other than copper. Makeup acid, used to redissolve scrap copper for return to the commercial cells for deposition, replenishes the weak electrolyte (a strong acid solution) for return to copper stripping. Sufficient steam, wash water, and makeup water are added to the circuit to offset water vaporized or carried off with evolved oxygen during electrowinning.

COPPER RAFFINATE pH ADJUSTMENT (FIG. C-9)

The nickel-bearing raffinate from copper LIX contains an excess of acid, which is neutralized with ammonia and made slightly basic before the nickel value can be removed. In addition to neutralization, tank aeration causes precipitation of Fe, Mn, Mg, and Al initially extracted from the nodules and carried with the raffinate. The precipitated metals are settled, centrifuged, and returned to the wash circuit before leaving the process as waste. The overflow raffinate containing some entrained precipitate overflows the settler and passes on to nickel LIX.

NICKEL LIQUID ION EXCHANGE-EXTRACTION (FIG. C-10)

The neutralized raffinate is filtered from the entrained precipitate, and then depleted of nickel by organic ion exchange

Table C-1.—Operating parameters for high-temperature and high-pressure H_2SO_4 leach process

Parameter and unit	Value
ORE PROCESSING (FIG. C-2)	
Feed rate, wet basis (330 days/yr; 24 hr/day) ..... tpd..	10,900
Feed size to leaching ..... mesh..	−65
Pulp density, solids ..... pct..	35-40
LEACHING (FIG. C-3)	
Temperature ..... ° C..	245
Pressure ..... atm..	35
Acid feed ..... pct H_2SO_4..	93
Recovery, pct:	
Co	90
Cu	95
Fe	1
Mn	5
Ni	95
Zn	90
Contact time ..... hr..	4
H_2SO_4 consumption ..... lb/lb nodules..	0.4
Leaching reactions:	
$NiO + H_2SO_4 \rightarrow NiSO_4 + H_2O$	
$CuO + H_2SO_4 \rightarrow CuSO_4 + H_2O$	
$CoO + H_2SO_4 \rightarrow CoSO_4 + H_2O$	
$MnO_2 + H_2SO_4 \rightarrow Mn SO_4 + H_2O + 0.5\ O_2$	
$Fe_2O_3 + 3H_2SO_4 \rightarrow Fe_2(SO_4)_3 + 3H_2O$	
SOLID-LIQUID SEPARATION (FIG. C-4)	
Number of stages	6
Efficiency ..... pct..	98
Underflow density ..... pct solids..	35-40
Wash ratio ..... kg/kg liquor..	2
PREGNANT LIQUOR pH ADJUSTMENT (FIG. C-5)	
Adjustment agent	$CaCO_3$
H_2SO_4 concentration, final ..... gpl..	0.5
Entrained solids ..... ppm..	≈100
COPPER LIQUID ION EXCHANGE (FIG. C-6)	
Extraction:	
Extractant	[1]LIX 64N
Number of stages	3
Organic-aqueous ratio	1:1
Metals extraction, pct:	
Co	0.1
Cu	99.5
Fe	.1
Mn	.1
Ni	.1
Zn	.1
Ammonia wash ..... pct NH_3..	25
Residual NH_3 in organic ..... gpl..	1
Stripping:	
Strip solution concentration, gpl:	
H_2SO_4	160
Ni (max)	10
Cu	40
Zn	5
Number of stages	2
Organic-aqueous ratio	3:1
Temperature ..... ° C..	40
Stripping, pct:	
Co	0.2
Cu	87
Ni	.9
Zn	100
COPPER ELECTROWINNING—COMMERCIAL (FIG. C-8)	
Current density ..... A/m^2..	180
Current efficiency ..... pct..	94
Temperature ..... ° C..	50
Cu in-out ..... gpl..	53-40
H_2SO_4 in-out ..... gpl..	160-180
COPPER RAFFINATE pH ADJUSTMENT (FIG. C-9)	
Number of stages	4
Precipitation agent	NH_3
Final pH	≈4.0

Parameter and unit	Value
NICKEL LIQUID ION EXCHANGE-EXTRACTION (FIG. C-10)	
Extraction:	
Extractant	[1]LIX 64N
Number of stages	3
Organic-aqueous ratio	5:1
Temperature ..... ° C..	40
Metals extraction, pct:	
Co	1
Cu	1
Ni	99.5
Washing (primary):	
Washing agent ..... pct NH_3..	1
Number of stages	3
Organic-aqueous ratio	3.3:1
Residual NH_3 in organic ..... gpl..	0.1
NICKEL LIQUID ION EXCHANGE-STRIPPING (FIG. C-11)	
Ammonia scrub (secondary):	
Wash composition, gpl:	
$(NH_4)_2SO_4$	200
H_2SO_4	1
Number of stages	2
Organic-aqueous ratio	1:1
Residual NH_3 in organic ..... gpl..	0.01
Temperature ..... ° C..	40
Nickel stripping:	
Strip solution composition, gpl:	
Cu	<0.001
H_2SO_4	40
Ni	50
Number of stages	3
Organic-aqueous ratio	5:1
Stripping, pct:	
Co	0.3
Cu	<.004
Ni	98.8
NICKEL ELECTROWINNING—COMMERCIAL (FIG. C-12)	
Current density ..... A/m^2..	180
Current efficiency ..... pct..	93
Temperature ..... ° C..	60
Ni in-out ..... gpl..	75-50
H_2SO_4 in-out ..... gpl..	0.016-40
Na_2SO_4 ..... gpl..	100
H_3BO_3 ..... gpl..	15
COBALT RECOVERY (FIG. C-13)	
Precipitating agent ..... pct NH_4HS..	30
Precipitation, pct:	
Co	98
Cu	99.9
Ni	99
Zn	99.9
Temperature ..... ° C..	80
Clarifier density ..... pct solids..	5
Wash ratio	2:1
Co leaching: slurry ..... pct..	40
Leaching agent ..... pct H_2SO_4..	70
Evaporation-crystallization water removal ..... pct..	70
Co oxidation:	
Temperature ..... ° C..	100
Pressure ..... psig..	150
Co reduction:	
Temperature ..... ° C..	175
Pressure ..... psig..	500
Reductant	H_2
AMMONIA RECOVERY (FIG. C-14)	
NH_3 absorber:	
Temperature ..... ° C..	35
Pressure ..... atm..	1.2
Number of stages	1
NH_3 stripper:	
Pressure ..... atm..	1.5
Recovery of NH_3 ..... pct..	99
Number of stages	2

[1]Reference to specific trade names does not imply endorsement by the Bureau of Mines.

extraction in three stages of pH-controlled countercurrent extraction. The nickel-depleted aqueous phase, containing primarily cobalt, proceeds to cobalt recovery The entrained aqueous, containing dissolved ammonia, extracted nickel, and trace metals, is removed from the organic phase in a liquid separation step. The ammonia removal requires two stages of recovery. The organic is countercurrently washed in two stages, and then the aqueous wash phase is steam stripped of ammonia.

NICKEL LIQUID ION EXCHANGE-STRIPPING (FIG. C-11)

The partially ammonia-stripped organic passes to a second step for reaction with H_2SO_4 to draw the remaining ammonia into an aqueous phase. The phases are countercurrently contacted and separated in two stages. The aqueous phase returns to nickel extraction. The organic phase, containing nickel and trace metal impurities, enters two countercurrent stages of nickel stripping with weak electrolyte from electrowinning. This electrolyte is heated passing to and cooled passing from nickel electrowinning which is operated at higher temperatures. Losses of the organic extractant during the stripping of nickel are replenished with fresh organic. A small amount of organic is purged to a trace metals removal step to prevent a buildup. The "cleaned" organic purge and makeup organic are combined with the nickel-free organic for recycle to the nickel LIX extraction step.

NICKEL ELECTROWINNING—COMMERCIAL (FIG. C-12)

Nickel is recovered from the strong electrolyte by electrowinning in a manner similar to that used for copper recovery. In nickel electrowinning, however, cathode bags are used, and the strong electrolyte is chemically conditioned with sodium sulfate and boric acid to control its conductivity and pH. Dissolved organic, carried from the LIX step, is adsorbed on activited carbon prior to any electrolyte passing to electrowinning. Nickel is recovered in a manner similar to that used for copper recovery. The starter sheets are pickled in H_2SO_4 prior to use in the commercial cells, and nickel scrap is dissolved in ammonia-containing raffinate and recycled to the ion exchange process. The electrolyte purge required to remove impurities from the electrowinning circuit passes to raffinate neutralization. The strongly acidic, weak electrolyte returns to the nickel stripping circuit.

COBALT RECOVERY (FIG. C-13)

Along with any unextracted Cu, Ni, and Zn, Co is recovered from the Ni LIX raffinate by precipitation with ammonium hydrosulfide (produced by sparging hydrogen sulfide into an excess of ammonia solution). The sulfide precipitate is separated from the raffinate in a clarifier. The clarifier overflow is filtered of entrained precipitate and sent to ammonia recovery. The underflow is mixed with electrolyte purges from Cu and Ni electrowinning as well as the Co recovered from stripping the LIX reagent. The mixture is pressure leached with air to preferentially dissolve the Ni and Co sulfides, leaving the Cu and Zn sulfides in the residue. The latter are removed by filtration and sold, as minor products, to smelters for recovery of metal values.

Following pH adjustment and reprecipitation with hydrogen sulfide for final removal of any Zn and Cu solubilized in the first leach, the Ni-Co sulfate solution is heated and autoclaved, and Ni is reduced with hydrogen. Sufficient ammonia solution is added during reduction to neutralize the acid formed. Only a portion of the nickel is removed per pass to prevent overreduction and subsequent contamination of the nickel powder with cobalt. After densification through repeated recycle, the nickel powder is removed, washed, and passed to drying and briquetting for sale.

The largely nickel-free cobalt sulfate solution passes to an evaporator-crystallizer where the remaining nickel and cobalt are precipitated as the double salts with ammonium sulfate. Excess ammonium sulfate is purged, and the salts are redissolved in strong ammonia solution. The cobalt in solution is oxidized to the cobaltic state (Co^{3+}) with air to allow cobalt to remain in solution. The stream is acidified to remove the nickel salts that are separated and recycled to the pH adjustment step. The nickel-free solution is then heated and autoclaved for removal of cobalt by hydrogen reduction. Sufficient ammonia is added to neutralize the acid generated. The cobalt powder is dried and briquetted for sale, and the ammonium sulfate is purged to ammonia recovery.

AMMONIA RECOVERY (FIG. C-14)

The raffinate from cobalt recovery, containing process ammonium sulfate and ammonia, is countercurrently contacted with slaked lime in a boil to recover the ammonia value of the sulfate. The precipitate from the lime boil enters a thickener, then overflows to the waste surge tank for disposal in a tailings pond. The overflow liquor is recycled to the CCD circuit. Steam sparged into the lime boil strips ammonia, which passes to a three-stage ammonia condenser-absorber circuit. The aqueous absorbed ammonia solution returns to the process. The vent gases of the entire process are passed through ammonia recovery. Unabsorbed vent gas is discharged to the stack for disposal.

PLANT SERVICES

Plant services include process and cooling water supply and treatment, steam raising and power generation, and stack gas treatment. Makeup water is clarified and softened for distribution to the process, as required. Additional treatment is required for cooling tower water makeup, boiler feed water makeup, and for supplying plant potable water. Offgas hydrogen from cobalt recovery along with coal is burned in the main boilers to raise the required process steam and generate a portion of the power required in the process. Following particulate removal, the flue gases are combined with other process offgases and pass to gas treatment, where sulfur oxides and other acidic constituents are removed by scrubbing with limestone. The scrubbed offgases are reheated (to avoid condensation of vapors), combined with scrubbed vents from ammonia recovery, and are passed to stacks for disposal.

MANGANESE PRODUCTION ADD-ON

The recovery of manganese from H_2SO_4 leach tails is an option that has been investigated. Recovery of manganese from the tailings would require dissolution of the residue and chemical manipulation to precipitate manganese as an oxide,

possibly MnO_2, involving several separation-purification steps. The MnO_2 could be used directly in steel production if specifications are met,or possibly could be used as a feed material to produce ferromanganese or other manganese alloys. The recovery of manganese from the process tails would be contingent on market conditions and process economics. Because of the relatively new technology required in manganese recovery from H_2SO_4 leach tails, and the dependency on economic and technical conditions, no detailed flowsheets are presented for this process.

PROCESS ALTERNATIVES

A major alternative to the proposed process configuration involves a low-temperature and low-pressure treatment of slurried nodules in acid solution, There are, however, major drawbacks, such as solubilization of an undesirable amount of Fe that would need to be removed, longer treatment time, and lower recovery of Ni, Cu, and Co.

Other than the metals separation and purification steps, the process configuration is based on the Moa Bay, Cuba, process, formerly operated by the Freeport Nickel Co., of New Orleans, La. In the absence of actual operating data, there is little reason to believe that nickel recovery from ocean floor nodules will differ significantly from nickel recovery in Moa Bay iron-laterite ores.

A slurry, whether produced from nodules or laterite ore, when leached at high temperature will substantially extract the metals of interest as well as undesirable trace metals in amounts depending on the source.The leach reactors are very fundamental in design and of proven operational reliability. The special alloy flash-down values used in this process are economically and mechanically feasible and present the most convenient arrangement.

The Cu raffinate neutralization step, which assumes the use of enough ammonia to generate a basic solution and oxidation of Co to prevent coextraction with Ni, could be eliminated if a reagent could be found to selectively remove Ni in the presence of Co. The precipitation and separation of basic salts of Fe, Mn, Mg, and Al would be eliminated, with a savings of necessary equipment.

The ammonium sulfate solutions purged from the LIX extraction and the copper raffinate neutralization have been treated with lime for the recovery of ammonia for recycle. An alternative approach would involve direct recovery of ammonia sulfate by evaporation-crystallization for sale as a byproduct. The alternative is highly energy intensive because of the number of crystallizing-evaporating steps necessary to produce a relatively pure byproduct from a stream containing many entrained process impurities. The production of ammonium sulfate is outside the interest of the process and could be severe on the local market, because this production would be approximately 15 pct of present U.S. production and could affect market prices.

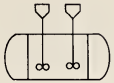
Alternative configurations of the metals separation steps are possible, such as selective extraction-selective stripping, but their impact on overall plant material and energy balances should be minor. Many variations are possible in the details of the scheme used for recovery of cobalt from a mixed sulfide precipitate. The impact on plant requirements would not differ appreciably from the present approach, because the sulfides will still be oxidized to sulfates, purged, and hydrogen reduced. It does not appear likely that the solution could be purified easily enough to permit recovery of electrolytic cobalt.

KEY

Absorber

Aerator

Agitator

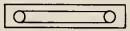


Autoclave

Blower

Centrifuge

Conveyor



Covered conveyor

Cyclone

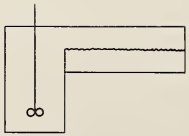
Ejector

Filter

Filter

Heat exchanger

Hopper



Mixer-settler

Pump

Surge tank

Surge tank, agitated

Thickener

Figure C-1.—Key to symbols.

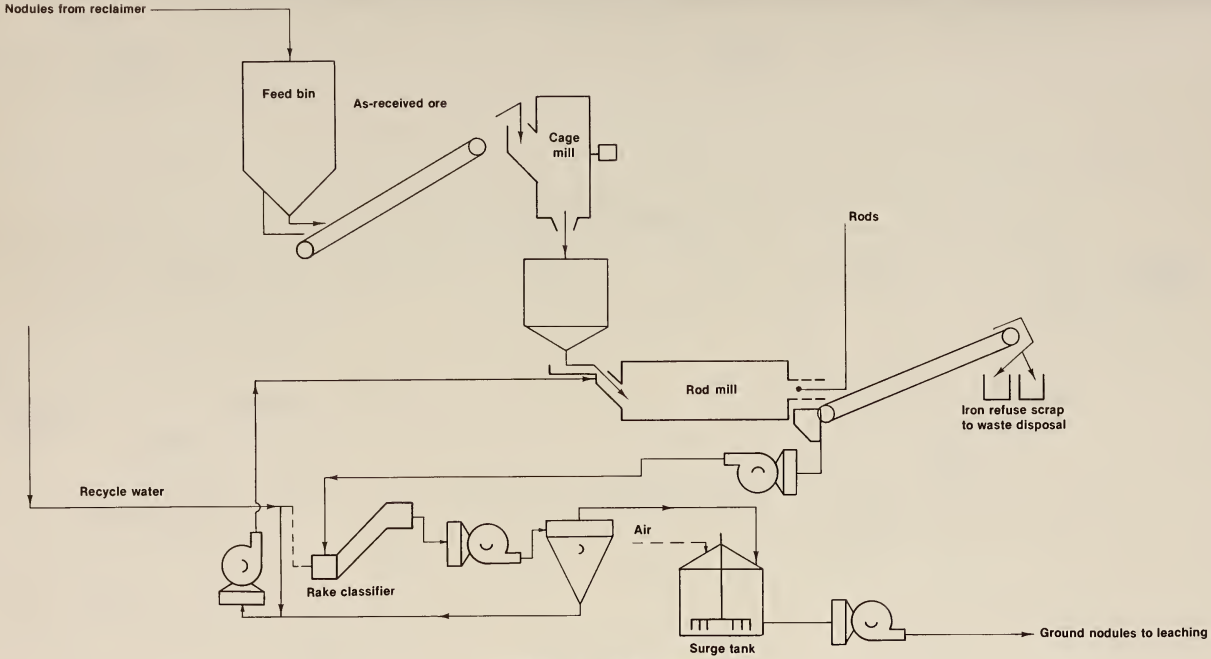


Figure C-2.—Ore processing.

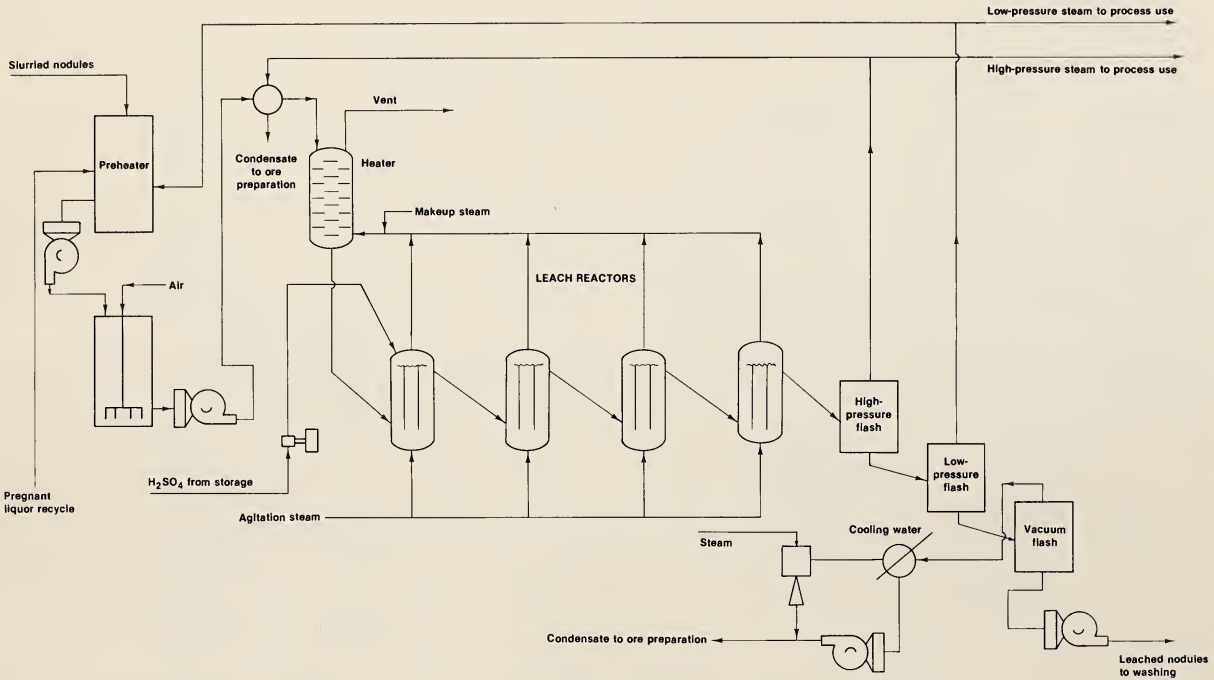


Figure C-3.—Leaching.

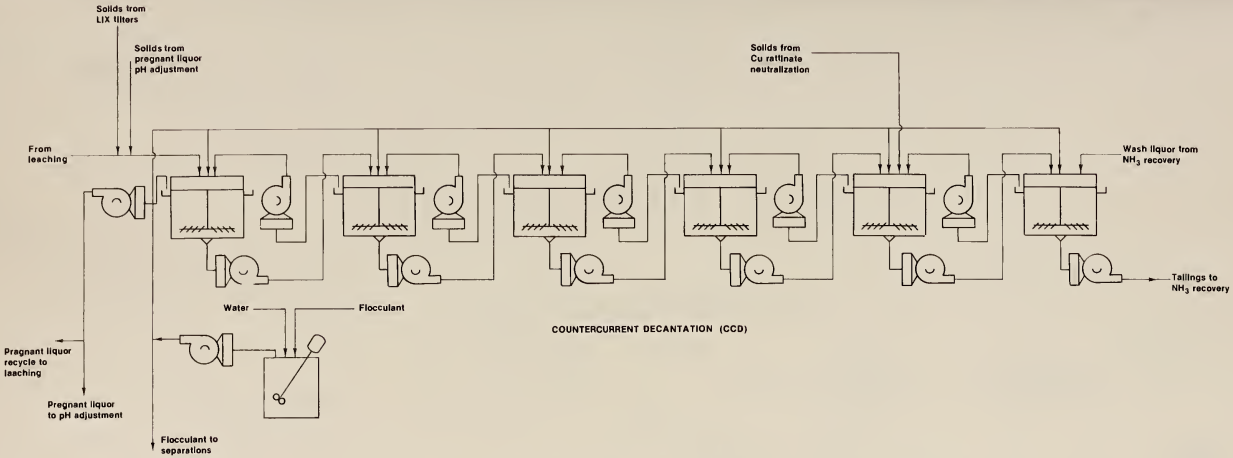


Figure C-4.—Solid-liquid separation.

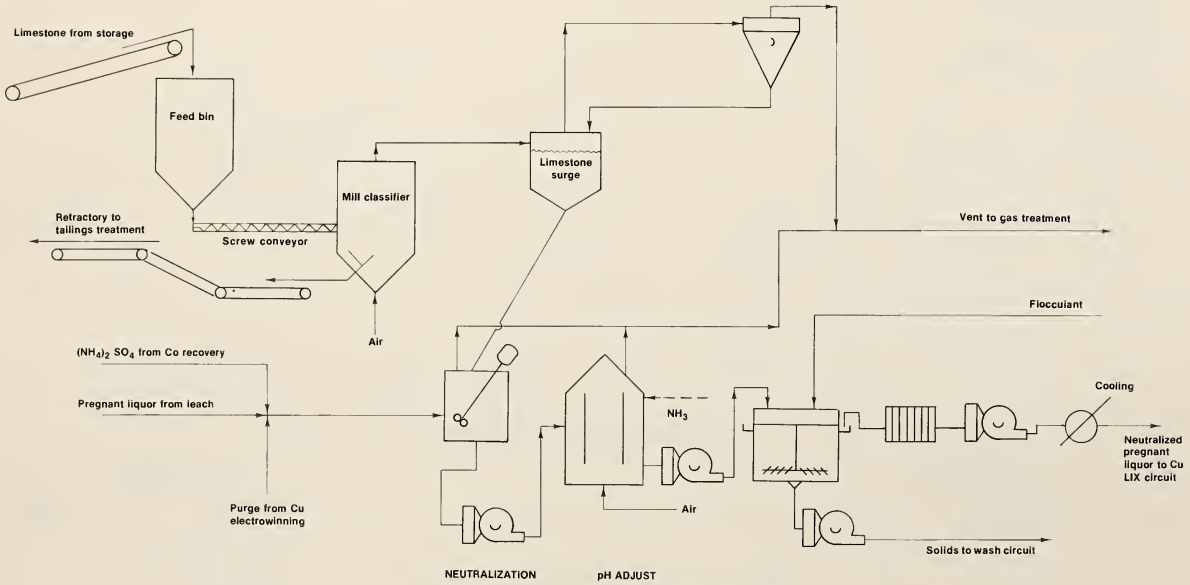


Figure C-5.—Pregnant liquor pH adjustment.

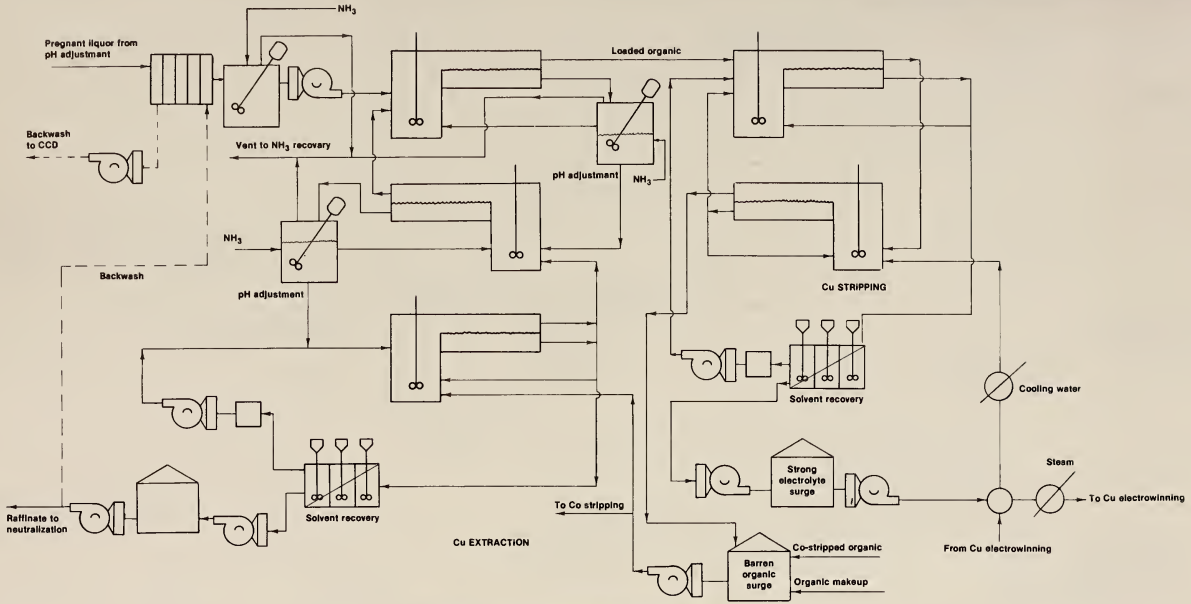


Figure C-6.—Copper liquid ion exchange.

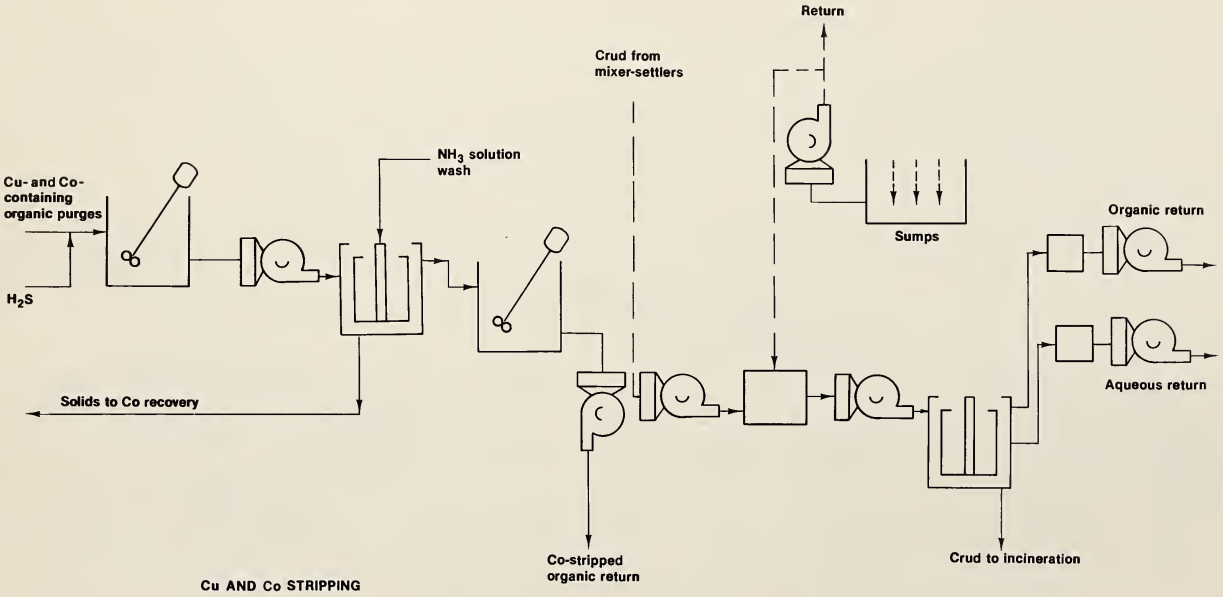


Figure C-7.—Cobalt stripping-organic purge.

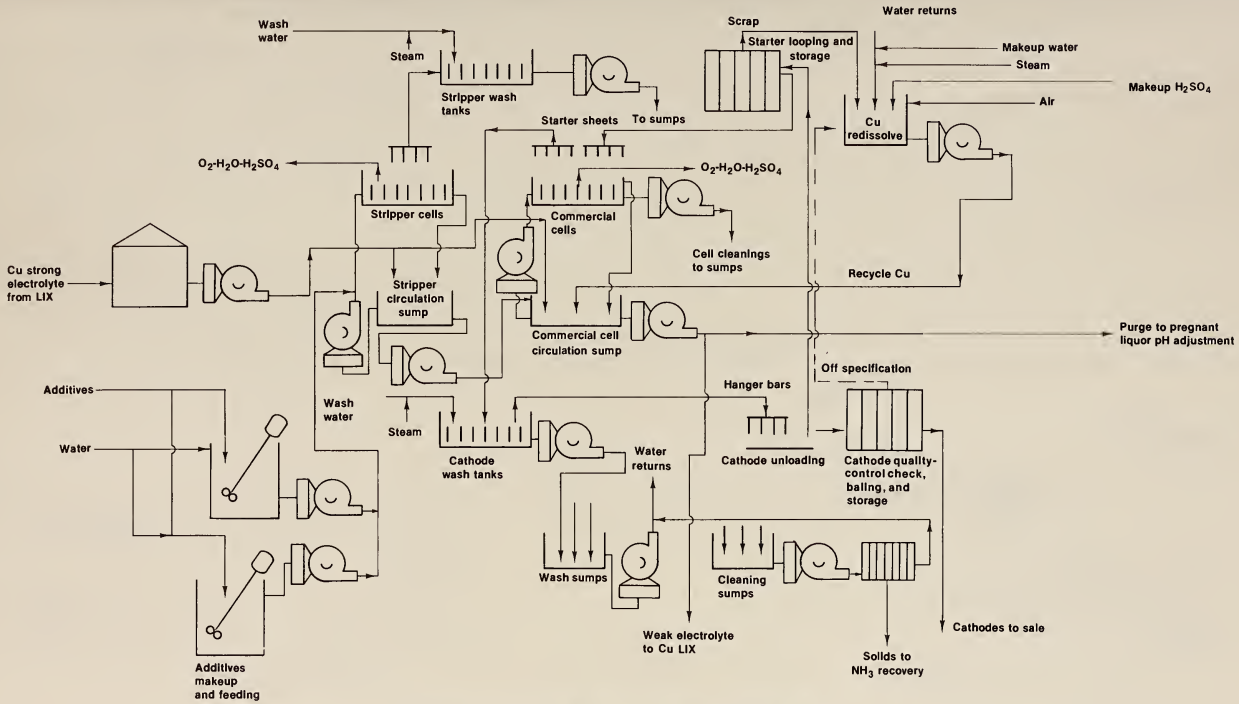


Figure C-8.—Copper electrowinning—commercial.

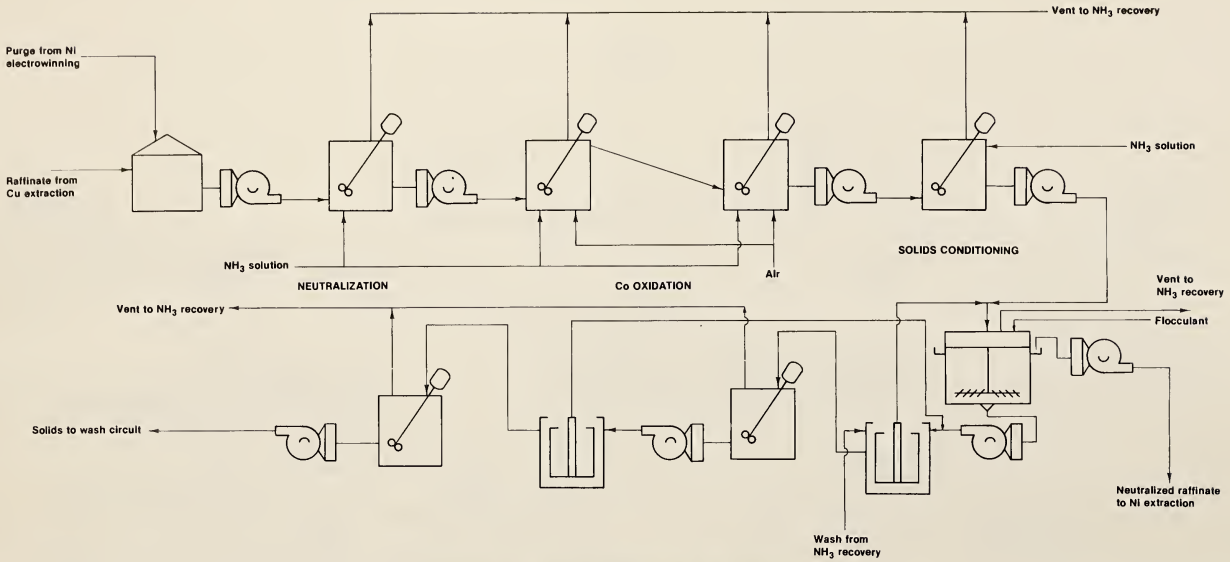


Figure C-9.—Copper raffinate pH adjustment.

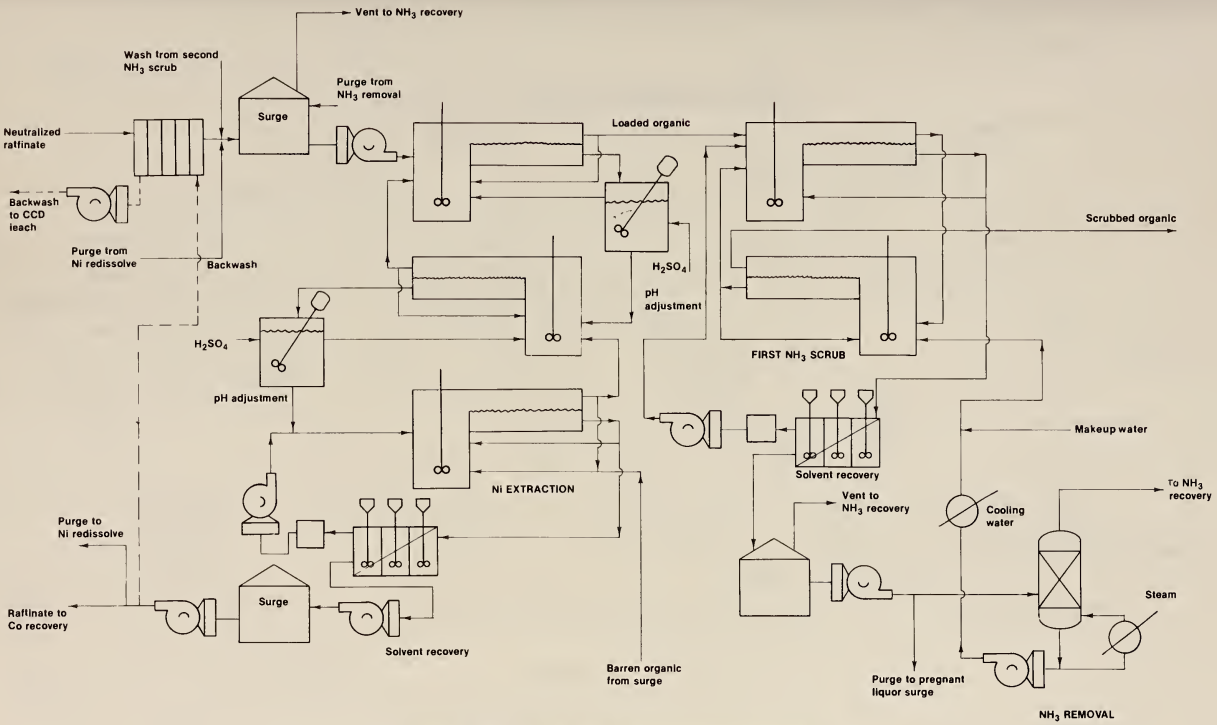


Figure C-10.—Nickel liquid ion exchange-extraction.

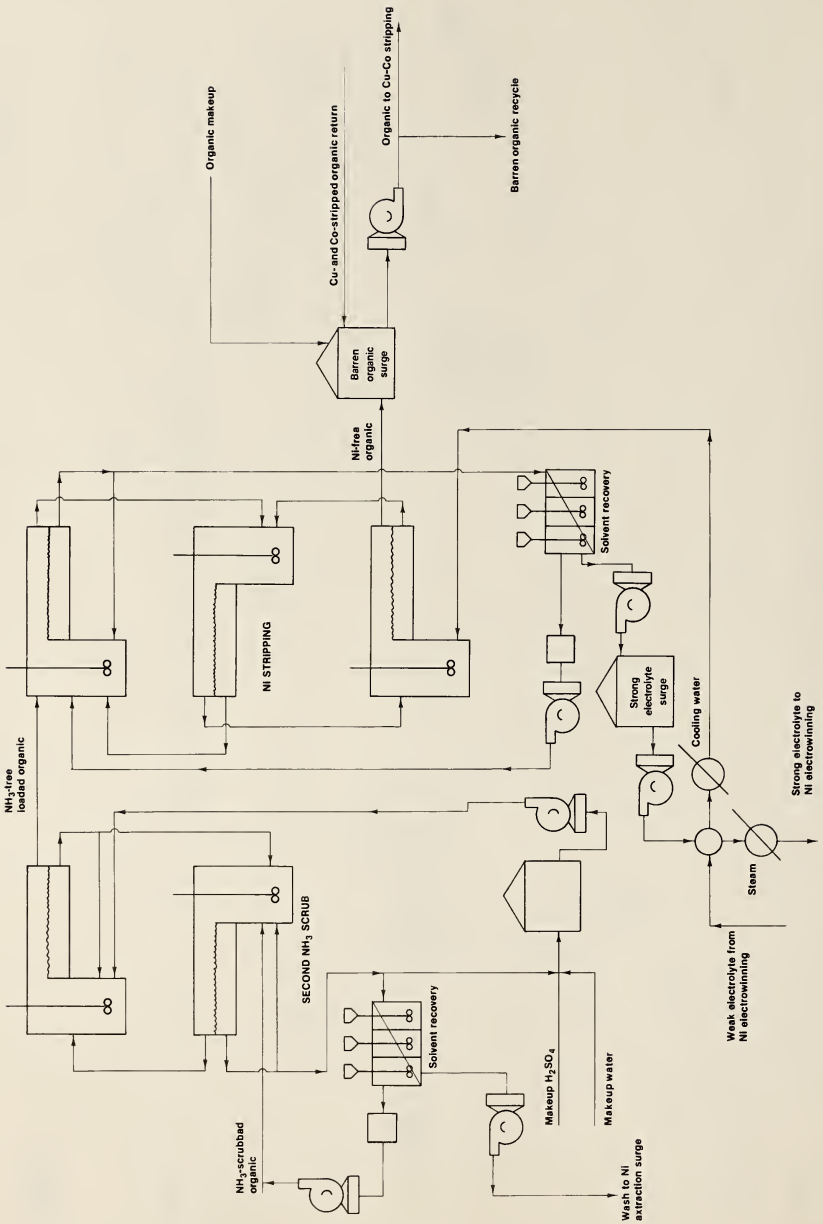


Figure C-11.—Nickel liquid ion exchange-stripping.

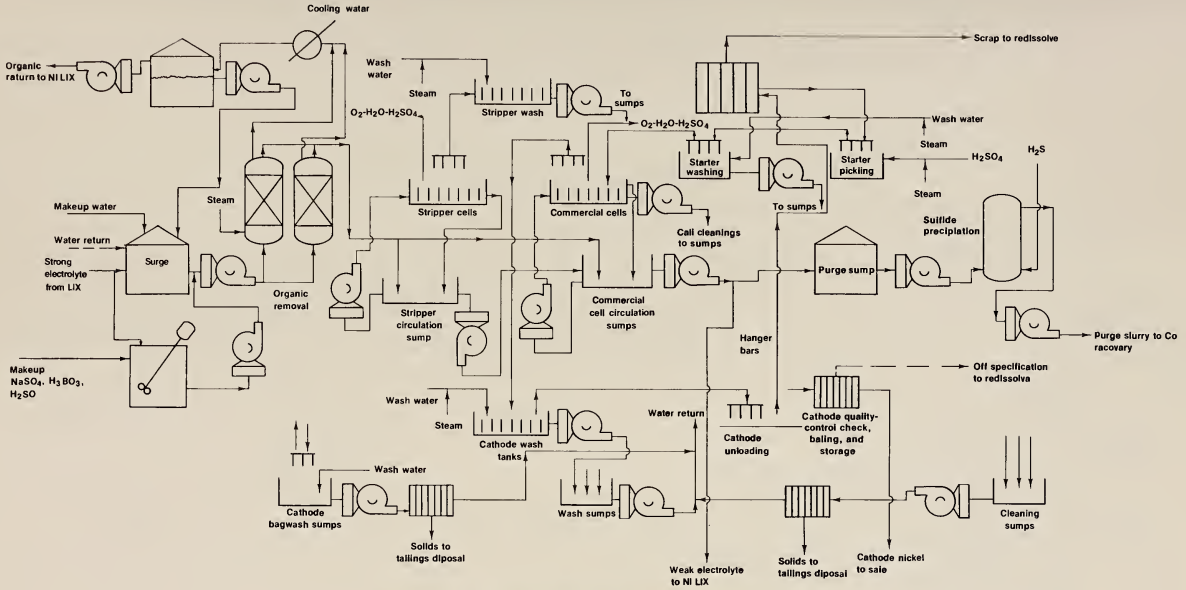


Figure C-12.—Nickel electrowinning—commercial.

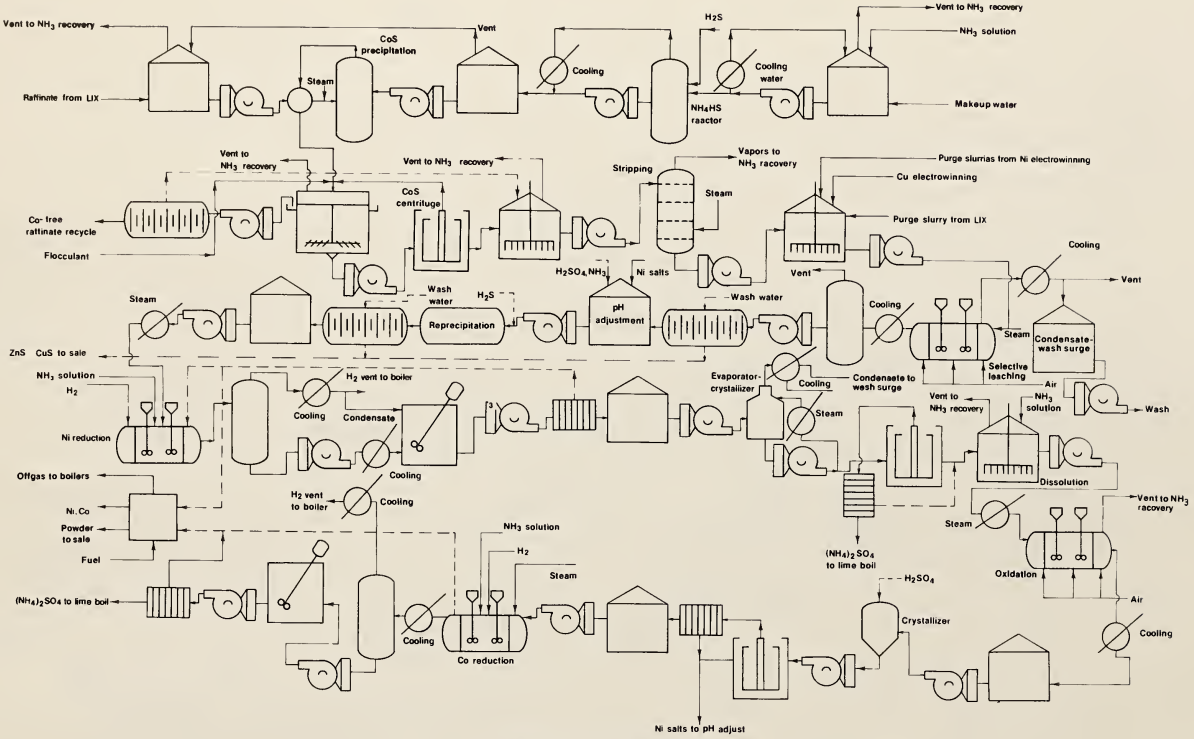


Figure C-13.—Cobalt recovery.

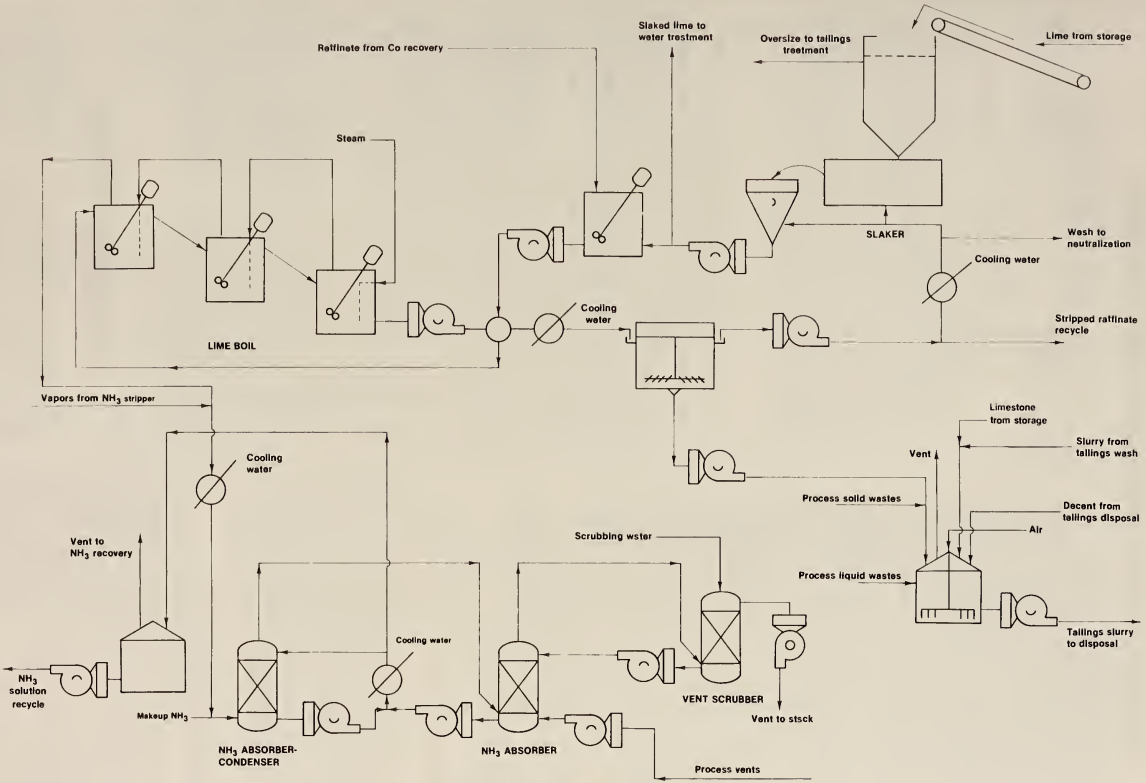


Figure C-14.—Ammonia recovery.

APPENDIX D.—REDUCTION AND HCl LEACH PROCESS

The reduction and HCl leach process is a four-metal process in which Mn, Cu, Ni, and Co are liberated from dried nodules by a high-temperature (500° C) gaseous hydrogen chloride treatment of nodules. Hydrogen chloride reduces manganese dioxide to manganous chloride (liberating chlorine gas) and also reacts with other metal oxides to form soluble chloride salts. A hydrolysis reaction and quench follow, where water is sprayed on the nodules and the iron is precipitated as ferric hydroxide. The nodules are leached with water and HCl, forming a concentrated pregnant liquor of chloride salts.

Copper is extracted by liquid ion exchange (LIX) reagents from the pregnant liquor, and is stripped and recovered as electrowon cathodes. Cobalt is solvent-extracted from the copper raffinate, stripped, and separated by precipitation with hydrogen sulfide. It is recovered from the sulfide precipitate, along with some Ni, Zn, and Cu, by selective leaching and hydrogen reduction. Nickel is extracted by LIX reagents from the cobalt raffinate, stripped, and recovered as electrowon cathodes. The nickel raffinate is evaporated, crystallizing manganese chloride as well as the other remaining chloride salts.

The salts are dried using combustion gases in a countercurrent dryer. The dried salts are charged to a high-temperature fused salts electrolysis furnace, where molten manganese metal is tapped and cast as product and chlorine gas is liberated. Excess hydrogen chloride gas in the process is recovered and recycled. Generated chlorine gas is recovered, dried, and delivered to a local chemical complex which, in exchange, returns makeup hydrogen chloride to the process.

Detailed descriptions of each segment of the process are given for the following flowsheets. A summary of operating parameters for each section is given in table D-1. A key to the flowsheet symbols is given in figure D-1.

ORE PROCESSING AND DRYING (FIG.D-2)

Wet nodules are reclaimed from storage and fed through a primary cage mill where they are reduced to minus 7/8 in. They then pass to a fluid-bed dryer where surface and pore water is removed at 175° C by direct contact drying with combustion gases. Bed overflow is reduced to minus 65 mesh in a secondary cage mill, and dryer and mill fines are removed from offgases by cyclones and an electrostatic precipitator. Offgases pass to gas treatment for scrubbing, while dried nodules are transferred hot in an enclosed conveyor to reduction.

HYDROCHLORINATION (FIG. D-3)

Dried nodules are reacted in a fluidized bed hydrochlorination reactor by contact with the hydrogen chloride gas from the HCl surge, which is preheated to 175° C. The exothermic reactions maintain the reactor at 500° C. Manganese dioxide is reduced to manganous chloride, and chlorine is produced. Essentially all the Cu, Ni, and Co, as well as 90 pct of the alkali and alkaline earths present in the nodules, react to form chloride salts. Approximately 100 pct excess HCl gas is used in the reaction. This HCl gas, as well as the chlorine and water liberated in the reaction are returned to HCl-Cl_2 recovery. The reduced-chlorinated nodules are delivered to a second fluidized bed where any iron chloride is hydrolyzed by a water-spray quench, forming insoluble ferric hydroxide, and the nodules are cooled to 200° C. The offgases from both fluidized beds are sent to a electrostatic precipitator system for dust removal. The hydrolysis offgas is also passed through a waste heat recovery system.

LEACHING AND WASHING (FIG. D-4)

The chlorinated nodules are leached with water and HCl in a tank where the soluble chlorides are dissolved to form a liquor with a pH of 2. The solution is cooled to 40° C by circulating the liquor through an external heat exchanger. The slurried nodules are washed countercurrently in a six-stage thickener circuit to remove 98 pct of all soluble metal values, forming a pregnant liquor. The wash water is recycled water from process water surge. Washed tailings are sent to the waste treatment area. Flocculant is added to the thickeners to improve the settling properties of the solids.

COPPER LIQUID ION EXCHANGE (FIG. D-5)

Pregnant liquor is filtered and passed to a three-stage countercurrent LIX extraction circuit where copper is removed from pregnant liquor. Some of the other chloride salts are physically entrained in the organic phase. These entrained chlorides are removed by washing with a water solution in a two-stage wash circuit. A purge from this wash solution is returned to the pregnant liquor surge, and makeup water is added to the circuit equal to this purge.

The copper is stripped from the organic by countercurrent contact in two stages at controlled pH with depleted electrolyte from copper electrowinning. Because electrowinning conventionally occurs at a higher temperature than the operation of the LIX circuit, the strip solution is heated passing to electrowinning and cooled passing from electrowinning.

Provision is made for periodically cleaning the mixer-settler units used in extraction and stripping and for recovering organic and aqueous phases for recycle. Degraded organic, dust, and other forms of "crud" are removed from the organic and incinerated.

Because a small amount of cobalt is coextracted and is not stripped with the copper, it must be removed from the LIX reagent to prevent its buildup. This is accomplished by precipitating the cobalt from a purge stream of organic with hydrogen sulfide. The precipitated solids are washed from the organic and passed to cobalt recovery, while the purified organic is returned to the extraction loop. Makeup organic is added to the stripped reagent to offset degradation and soluble organic losses to pregnant liquor and water wash, and the metal-free organic is recycled to extraction.

COPPER ELECTROWINNING—COMMERCIAL (FIG. D-6)

Cathode copper is recovered from the strong electrolyte from LIX using conventional technology. Starter sheets deposited on titanium blanks from strong electrolyte are removed, washed, looped, and returned to the commercial section as starters. Full-term cathodes produced in the commercial section are washed, unloaded, and prepared for shipment to sale. The major part of the weak electrolyte is recycled to the LIX section for stripping

Table D-1.—Operating parameters for reduction and HCl leach process

Parameter and unit	Value
ORE PROCESSING AND DRYING (FIG. D-2)	
Feed rate, wet basis (330 days/yr; 24 hr/day) ..... tpd	3,640
Feed size to reduction ..... mesh	-65
Drying temperature ..... ° C	150
HYDROCHLORINATION (FIG. D-3)	
Temperature ..... ° C	500
Pressure ..... atm	1
Reagent	HCl
Reactions:	
$MnO_2 + 4\ HCl \rightarrow MnCl_2 + 2H_2O + Cl_2$	
$Fe_2O_3 + 6HCl \rightarrow 2FeCl_3 + 3H_2O$	
$CuO + 2HCl \rightarrow CuCl_2 + H_2O$	
$NiO + 2HCl \rightarrow NiCl_2 + H_2O$	
$Co_2O_3 + 6HCl \rightarrow 2CoCl_2 + 3H_2O + Cl_2$	
Hydrolysis:	
Temperature ..... ° C	200
Pressure ..... atm	1
Hydrochlorination, pct:	
Co	100
Cu	96
Fe	27
Mn	94
Mo	96
Ni	100
LEACHING AND WASHING (FIG. D-4)	
Final pH	2
Underflow density ..... pct solids	15
Wash ratio	2:1
Number of stages	6
Soluble metals removed ..... pct	98
COPPER LIQUID ION EXCHANGE (FIG. D-5)	
Extraction:	
Extractant	[1]Kelex 100
Cu feed ..... gpl	≈8
Number of stages	3
Organic-aqueous ratio	2:1
Cu extraction ..... pct	99.5
Washing:	
Wash composition	H_2O
Number of stages	2
Organic-aqueous ratio	3:1
Temperature ..... ° C	40
Metals extraction, pct:	
Co	99.5
Cu	99.5
Ni	99.5
pH (with NaOH)	4
Stripping:	
Strip solution composition, gpl:	
H_2SO_4	160
Cu	40
Number of stages	2
Organic-aqueous ratio	4:1
Cu stripping ..... pct	95
Temperature ..... ° C	40
COPPER ELECTROWINNING—COMMERCIAL (FIG. D-6)	
Current density ..... A/m^2	180
Current efficiency ..... pct	94
Temperature ..... ° C	50
Cu in-out ..... gpl	53-40
H_2SO_4 in-out ..... gpl	160-180
pH ADJUSTMENT AND COBALT EXTRACTION (FIG. D-7)	
Cu raffinate pH adjustment:	
pH adjustment agent	NaOH
Number of stages	1
Final pH	4
Co liquid ion exchange extraction:	
Extractant	TIOA
Number of stages	3
Organic-aqueous ratio	2:1
Metals extraction, pct:	
Co	99
Cu	100

Parameter and unit	Value
pH ADJUSTMENT AND COBALT EXTRACTION (FIG. D-7)—Con.	
Metals extraction, pct—Con.	
Mn	10
Ni	0
Zn	99.5
Co stripping:	
Stripping solution pH	4
Number of stages	2
Organic-aqueous ratio	5:1
Stripping, pct:	
Co	99
Mn	99
Co recovery:	
Precipitating agent	H_2S
Precipitation ..... pct	100
Temperature ..... ° C	80
Pressure ..... atm	1
NICKEL LIQUID ION EXCHANGE (FIG. D-8)	
Extraction:	
Extractant	[1]Kelex 100
Number of stages	2
Organic-aqueous ratio	2:1
Temperature ..... ° C	40
Metals extraction, pct:	
Ni	99.5
Co	99.5
Cu	99.5
pH (with NaOH)	4
Washing:	
Washing agent	H_2O
Number of stages	2
Stripping:	
Strip solution composition, gpl:	
H_2SO_4	40
Ni	50
Number of stages	2
Organic-aqueous ratio	6:1
Ni stripping ..... pct	99
NICKEL ELECTROWINNING—COMMERCIAL (FIG. D-9)	
Current density ..... A/m^2	180
Current efficiency ..... pct	93
Temperature ..... ° C	60
Ni in-out ..... gpl	75-50
H_2SO_4 in-out ..... gpl	0.016-40
Na_2SO_4 ..... gpl	100
H_3BO_3 ..... gpl	15
MANGANESE RECOVERY (FIG. D-10)	
Trace elements removal agent	H_2S
Evaporation-crystallization water removal ..... pct	99.9
Fused salt electrolysis:	
Mn recovery ..... pct	90
Temperature, metal ..... ° C	1,300
Temperature, salt ..... ° C	800
Current density ..... A/m^2	46
COBALT RECOVERY (FIG. D-11)	
Slurry feed, solids ..... pct	40
Evaporation-crystallization water removal ..... pct	70
Co oxidation:	
Temperature ..... ° C	100
Pressure ..... psig	150
Co reduction:	
Temperature ..... ° C	175
Pressure ..... psig	500
Reductant	H_2
Leaching agent ..... pct H_2SO_4	70
HCl RECOVERY (FIG. D-12)	
HCl absorbing agent	H_2O
Gas drying agent	H_2SO_4
WASTE RECOVERY (FIG. D-13)	
Recovery agent	Slaked lime
NH_3 recovery ..... pct	99

[1]Reference to specific trade names does not imply endorsement by the Bureau of Mines.

A small amount of nickel is stripped along with the copper not deposited in electrowinning, and must be purged from the system. The purged electrolyte passes through purification cells where copper is removed by electrowinning to depletion. The decopperized electrolyte is sent to cobalt recovery for further processing. Makeup acid is used to redissolve scrap copper for return to the commercial cells for deposition, and sufficient steam, wash water, and makeup water are added to the circuit to offset water vaporized or carried off with evolved oxygen during electrowinning.

pH ADJUSTMENT AND COBALT EXTRACTION (FIG. D-7)

The raffinate from copper extraction is adjusted in a surge tank to a pH of 4 by the addition of NaOH solution. This stream then passes to a two-stage countercurrent solvent extraction circuit where cobalt is extracted as a tetrachloro-complex by the organic reagent. The preferred organic reagent is a tertiary amine such as tri-isooctylamine (TIOA). The cobalt is stripped from the organic by countercurrent extraction contact in two stages with recycled process water. Because of the high manganese concentration in the raffinate, a portion of it is extracted with the cobalt. The cobalt is separated by addition of hydrogen sulfide, which reacts to form cobalt sulfide precipitate which is centrifuged from the liquor and sent to cobalt recovery. The liquor, which is basically manganese chloride solution, is sent to manganese recovery.

NICKEL LIQUID ION EXCHANGE (FIG. D-8)

Nickel is recovered in a manner similar to that used in copper extraction. The cobalt-free raffinate passes to a three-stage countercurrent LIX extraction circuit where nickel is removed from the raffinate. Sodium hydroxide solution is added at interstages to keep the pH at 4 to ensure good nickel extraction. The loaded organic is washed to remove chloride in a two-stage operation. The nickel is stripped from the organic by countercurrent contact in two stages with depleted electrolyte from nickel electrowinning. Because electrowinning conventionally occurs at a higher temperature than the LIX circuit, the strip solution is heated-cooled passing to-from electrowinning.

Provisions are also made for cleaning the mixer-settler units and sending the resultant "crud" to incineration. An organic purge is also taken to ensure against buildup of unstrippable metals in the organic. Makeup organic is added to the stripped reagent to offset degradation and soluble organic losses.

NICKEL ELECTROWINNING—COMMERCIAL (FIG. D-9)

Nickel is recovered from the strong electrolyte by electrowinning in a manner similar to that used for copper recovery. In nickel electrowinning, however, cathode bags are used, and sodium sulfate and boric acid are added to the electrolyte to control its conductivity and pH. Dissolved organic carried from the LIX step is removed by adsorption on activated carbon prior to any electrolyte passing to electrowinning. Also, the starter sheets are pickled in H_2SO_4 prior to use in the commercial cells, and nickel scrap is redissolved in HCl-containing raffinate and the solution recycled to the cobalt-free raffinate surge. The electrolyte purge, required to remove impurities from the electrowinning circuit, passes to a sulfide precipitation reactor and then to cobalt recovery for retrieval of metal values.

MANGANESE RECOVERY (FIG. D-10)

The raffinate from nickel extraction is combined with the wash from cobalt extraction, and these are reacted with hydrogen sulfide to precipitate any remaining metal values that may have passed through the series of extractions. These precipitates are sent to cobalt recovery. The resultant solution is evaporated in a triple-effect evaporator using steam as the initial heat source. The overhead water is cooled and sent to the process water surge for recycle. The wet crystallized chloride salts are sent to a dryer, where the salts are passed countercurrently with combustion gases to drive off the remaining surface water as well as any water of hydration. The vent from the dryer is sent to gas treatment. The dried salts are conveyed in covered systems to a surge, which is blanketed with inert nitrogen gas to prevent reabsorption of water.

From this surge, the salts are fed to a high-temperature (1,300° C) fused-salt electrolysis furnace where molten manganese forms and collects at the bottom of the reactor. The manganese is tapped periodically and cast into molds and sold as metal product. Chlorine gas that evolves from the electrolytic reaction is collected, cooled by a water quench, and sent to HCl-Cl_2 recovery. Fused salts are also tapped from the reactor. These salts are mold cooled and sent to the waste disposal area. A certain amount of the manganese that does not pass inspection is recycled to the furnace with additives that assist in carrying out a complete recovery of the manganese. The lining of the reactor is cooled to prolong its life in this harsh environment. Areas surrounding the furnace are hooded, and constant venting is maintained to collect fugitive fumes from the furnace and the products tapped from the furnace. The graphite anode is also continuously replaced.

COBALT RECOVERY (FIG. D-11)

Several streams are merged to form the input to the cobalt recovery scheme. These are the slurry from Co extraction, purge from Mn recovery, the purges from Cu and Ni electrowinning, and the solids from organic stripping in Cu and Ni extraction circuits. The mixture is pressure leached with air to preferentially dissolve the Ni and Co sulfides, leaving the Cu and Zn sulfides in the residues. The latter are removed by filtration and sold, as minor products, to smelters for recovery of metal values.

Following pH adjustment and reprecipitation with hydrogen sulfide for final removal of any Zn and Cu solubilized in the first leach, the Ni-Co sulfate solution is heated and autoclaved, and Ni reduced with hydrogen. Sufficient ammonia solution is added during reduction to neutralize the acid formed. Only a portion of the nickel is removed per pass, to prevent overreduction and subsequent contamination of the nickel powder with cobalt. After densification through repeated recycle, the nickel powder is removed, washed, and passed to drying and briquetting for sale.

The largely nickel-free cobalt sulfate solution passes to an evaporator-crystallizer where the remaining nickel and cobalt are precipitated as the double salts with ammonium sulfate. Excess ammonium sulfate is purged, and the salts are redissolved in strong ammonia solution. The cobalt in solution is oxidized to the cobaltic state (Co^{3+}) with air. This permits the cobalt to remain in solution when the stream is acidified to

remove the nickel salts, which are then separated and recycled to the pH adjustment step. The nickel-free solution is then heated and autoclaved for removal of cobalt by hydrogen reduction. Sufficient ammonia is added to neutralize the acid generated. The cobalt powder is dried and briquetted for sale, and the ammonium sulfate is purged to the lime boil.

HCl RECOVERY (FIG. D-12)

The offgas from the hydrochlorination reactor contains a mixture of unreacted HCl, chlorine, and water. The HCl is absorbed by water, forming a highly concentrated aqueous HCl solution. The overhead gas from the tower is combined with the offgas from electrolysis and is dried by passing through a H_2SO_4 solution, which strongly absorbs the water from the gas, leaving dry chlorine for delivery as product. The HCl gas from the hydrolysis reactor is absorbed in the second tower, producing strong HCl solution. The offgas from this tower is mainly humid air and is sent to gas treatment. In both absorption towers, the dissolution of HCl is highly exothermic, and the heat is removed with cooling water.

A series of lean HCl vents is scrubbed to remove the last remaining HCl in a third tower. The overhead gas from this tower is also sent to gas treatment. All the HCl solutions are combined with H_2SO_4, and the HCl is stripped and sent to a HCl surge, where makeup HCl is added. The HCl is then sent to the hydrochlorination reactor. The bottoms from the HCl stripper are sent to a water stripper, where water is taken overhead and condensed. The remaining H_2SO_4 is filtered to remove any particulate matter that may have been entrained in the gas streams entering the HCl recovery section. The resulting strong H_2SO_4 is recycled. An aqueous HCl stream is split from the main aqueous HCl stream to provide acid streams needed at various stages in the process. Excess water developed in HCl recovery is returned to the process water surge.

WASTE RECOVERY (FIG. D-13)

Ammonia is recovered from the ammonia sulfate purges from cobalt recovery by reaction with slaked lime. Steam is blown into the mixture to strip the evolved ammonia. The vapor is combined with other ammonia vents, and they are scrubbed with water to form an aqueous ammonia solution that is returned to the aqueous ammonia storage for recycle within the process. The gypsum slurry from the lime boil is cooled and combined with the slurry from stack gas treatment. After liquid-solid separation in a thickener, the solids are combined with other process solid and liquid wastes and plant runoff, treated for pH control as required, and pumped to the tailings impoundment area for disposal. The overflow from the thickener is returned to the process water surge, where it is combined with other water returns and makeup water to satisfy the process water needs.

PLANT SERVICES

Plant services include process and cooling water supply and treatment, steam raising and power generation, stack gas treatment, and combustion gas preparation. Makeup water is clarified and softened for distribution to the process, as required. Additional treatment is required for cooling tower water makeup, boiler feed water makeup, and for supplying plant potable water. Process combustible wastes are burned along with coal in the main boilers to raise the required process steam and generate a portion of the power required in the process. Following particulate removal, the flue gases are combined with other process offgases and pass to gas treatment, where sulfur oxides and other acidic constituents are removed by scrubbing with limestone. The scrubbed offgases are combined with scrubbed vents from ammonia recovery and are passed to stacks for disposal.

PROCESS ALTERNATIVES

While data on the reduction of nodules with HCl and subsequent recovery of metal values from acid chloride solution have been reported in the patent literature, this technology currently has no direct analog in commercial extractive metallurgy. Also, while the thermodynamics of the reduction step are well known, and reports on laboratory studies of some separations of metals from chloride solutions are available, no data exist to indicate the expected properties of the nodule residues (e.g., filtering rates) or the problems associated with recovering a salable manganese metal from impure chloride solutions. Thus, the proposed process configuration has been established based on literature data that contain little detailed engineering and design information and without the benefit of insights that might be gained from analogies to conventional technology in related operations. This means that alternative process configurations might well be technically and economically more attractive, but access to more data would be required to make such a judgment.

A major process alternative is to use a low-temperature aqueous reduction and HCl leach. The stoichiometry of the reactions would consume the same amount of HCl as the high-temperature gaseous reduction. However, the iron would be dissolved as ferric chloride and would necessitate more expensive solvent extraction steps to remove the iron before recovering the valuable metals products and a spray roast of the resulting iron chloride solution to recover the HCl. On the positive side,an aqueous process would not require the drying step.

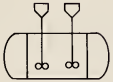
A number of possible alternatives is available for recovering manganese. Direct electrowinning of manganese has been proposed, but it is questionable that the final pregnant liquor would be pure enough to develop a good electrowon product. A cementation on aluminum to obtain manganese has also been proposed. The resulting aluminum would be spray roasted to recover HCl and form Al_2O_3 as a product, which must be sold or disposed. In addition, the manganese product may be contaminated with aluminum. Other schemes propose producing manganese hydroxide as a product which, in effect, sidesteps the problem of obtaining a pure metal product.

A number of metal separation schemes are possible. These include using different organic reagents as solvent extractants or LIX reagents.

Absorber

Aerator

Agitator

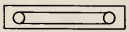


Autoclave

Blower

Centrifuge

Conveyor



Covered conveyor

Cyclone

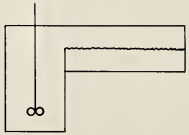
Ejector

Filter

Filter

Heat exchanger

Hopper

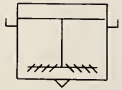


Mixer-settler

Pump

Surge tank

Surge tank, agitated



Thickener

Figure D-1.—Key to symbols.

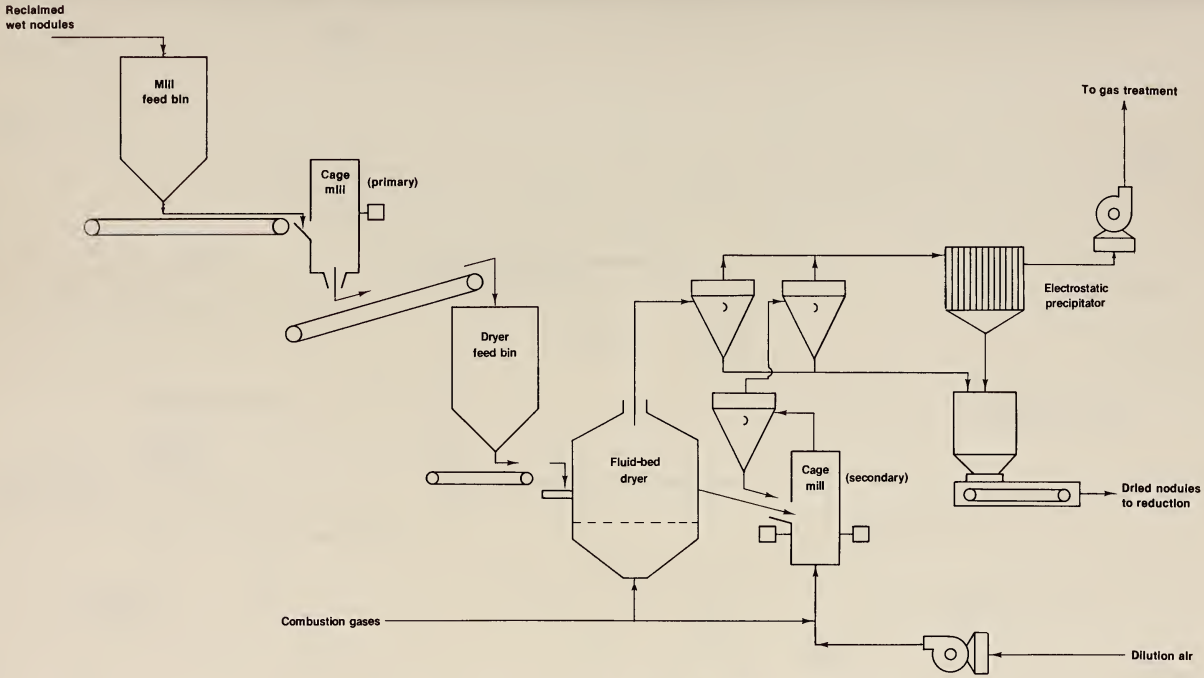


Figure D-2.—Ore processing and drying.

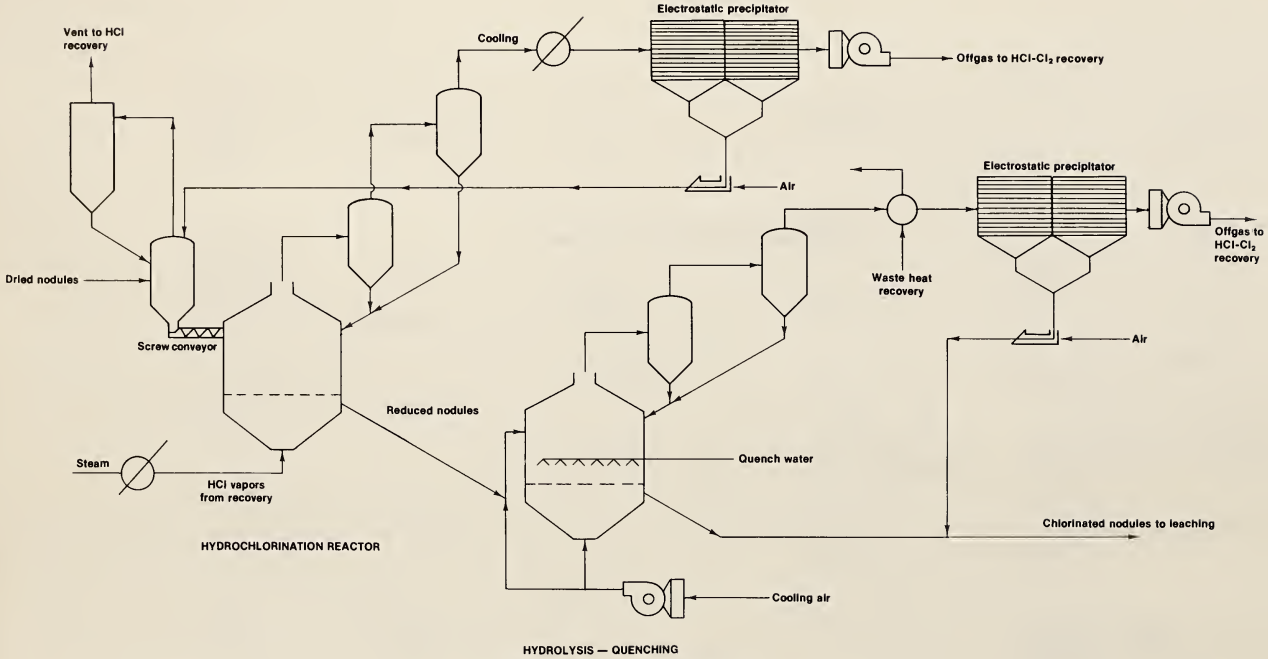


Figure D-3.—Hydrochlorination.

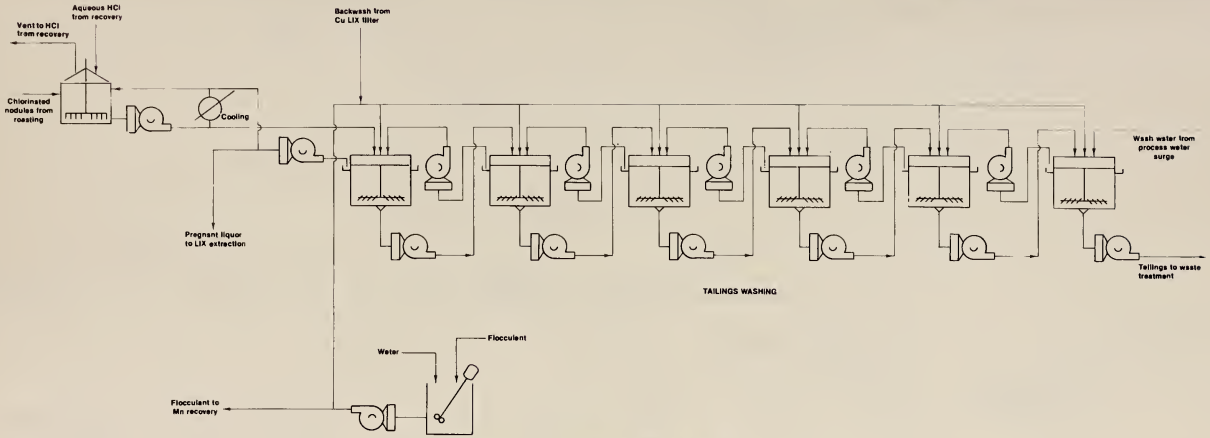


Figure D-4.—Leaching and washing.

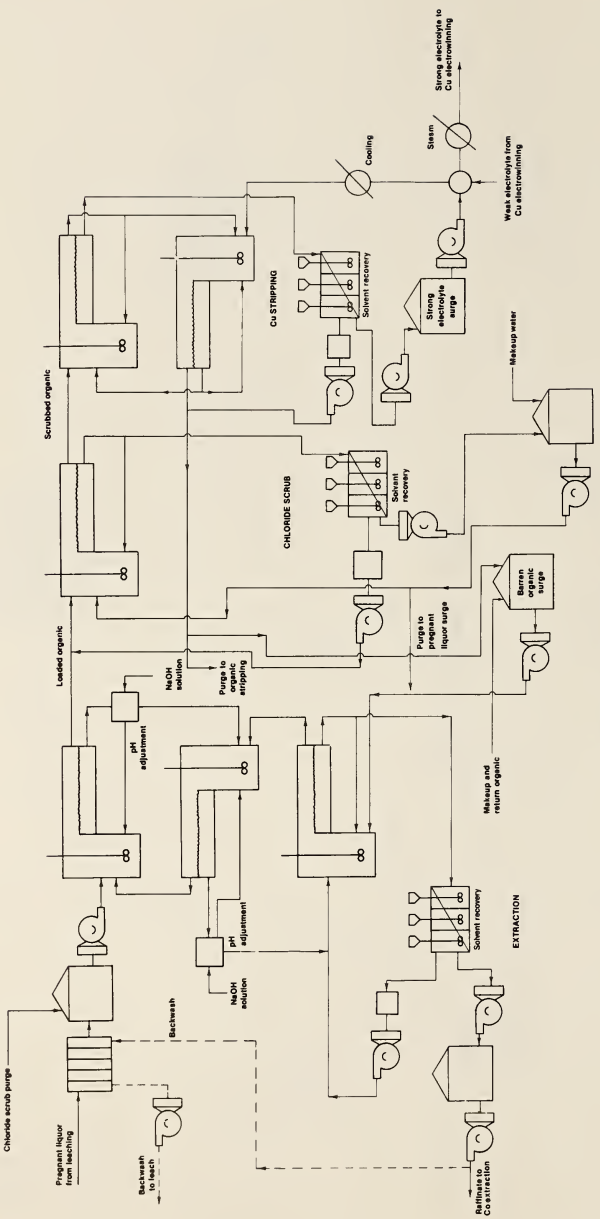


Figure D-5.—Copper liquid ion exchange.

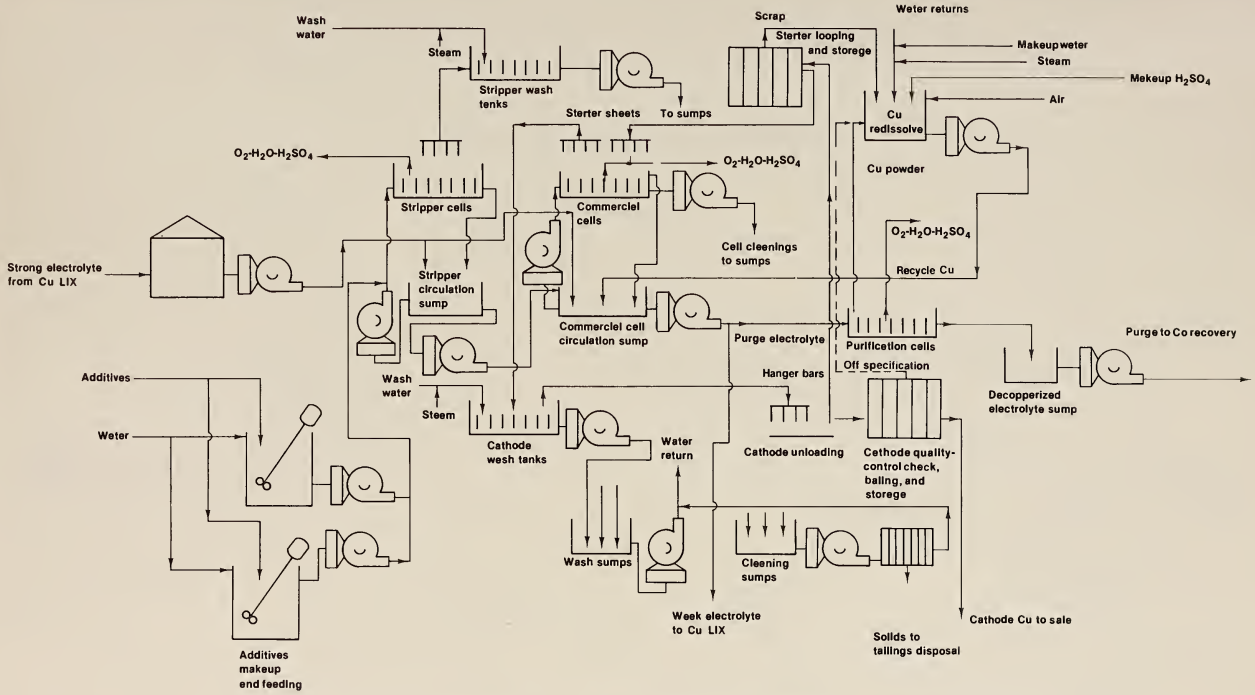


Figure D-6.—Copper electrowinning—commercial.

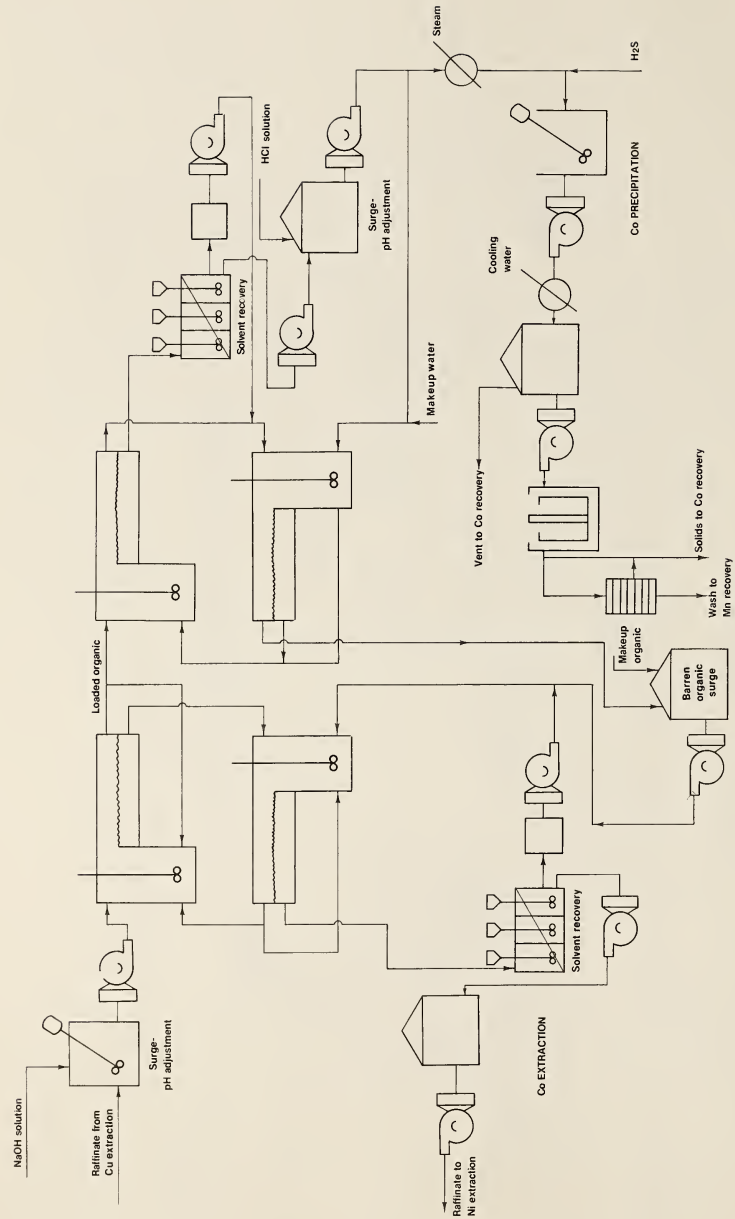


Figure D-7.—pH adjustment and cobalt extraction.

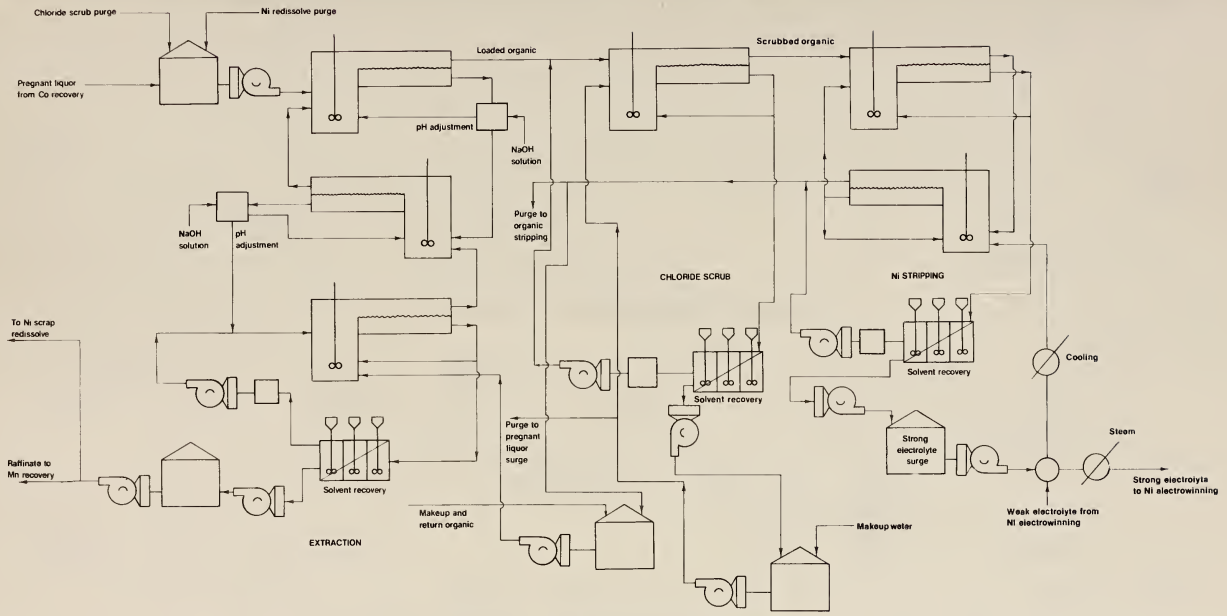


Figure D-8.—Nickel liquid ion exchange.

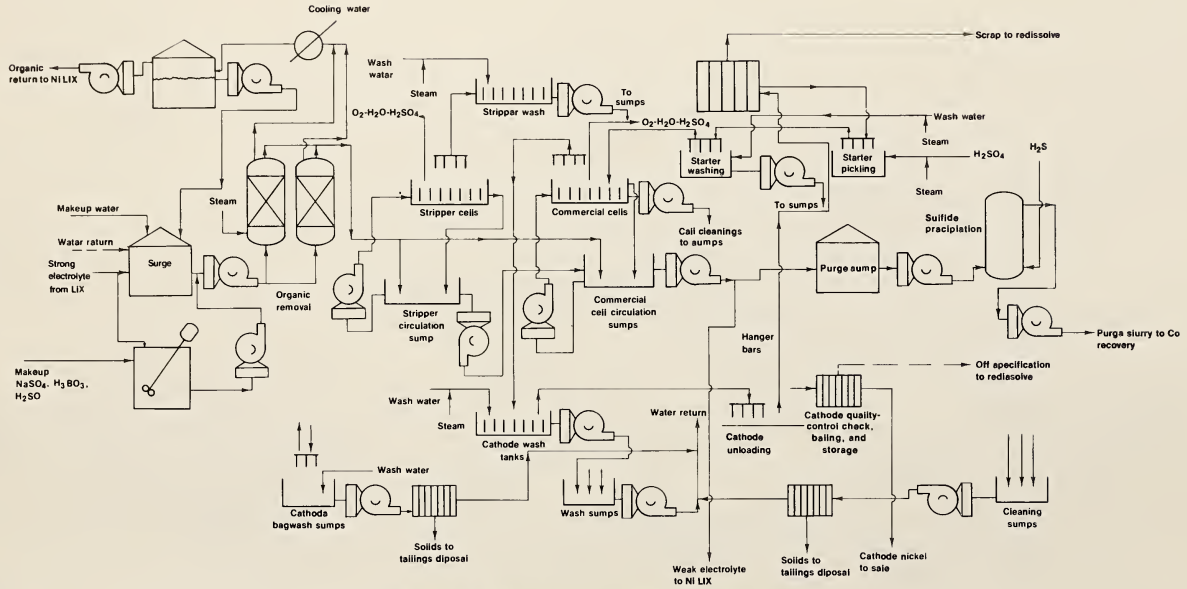


Figure D-9.—Nickel electrowinning—commercial.

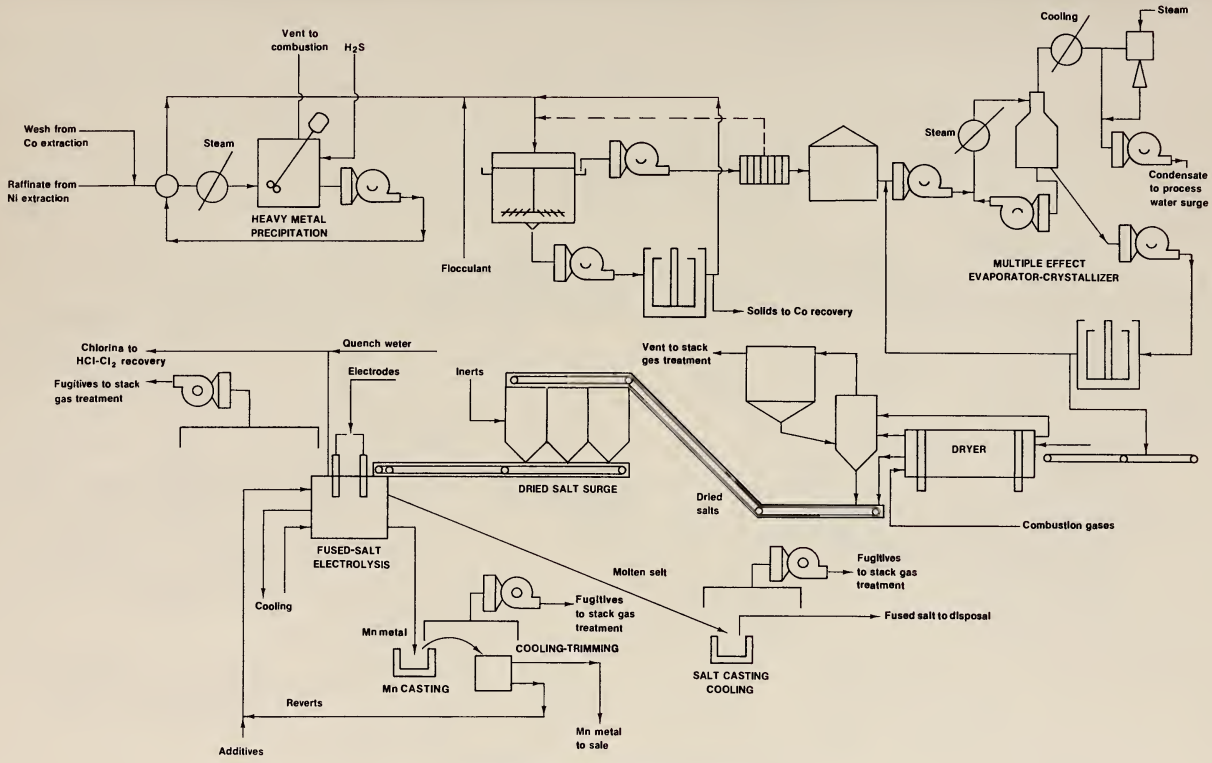


Figure D-10.—Manganese recovery.

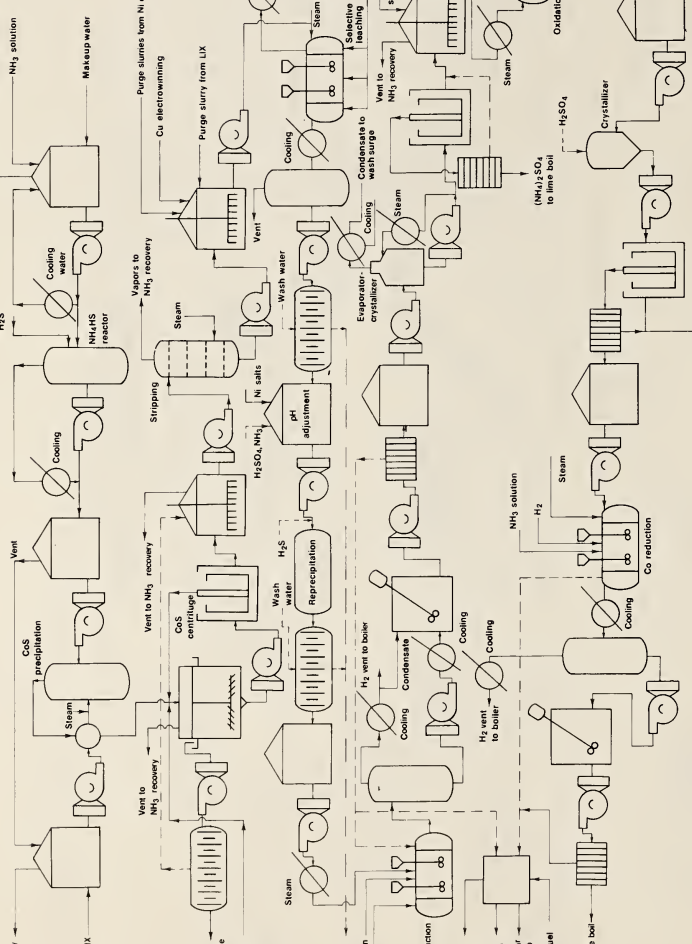


Figure D-11.—Cobalt recovery.

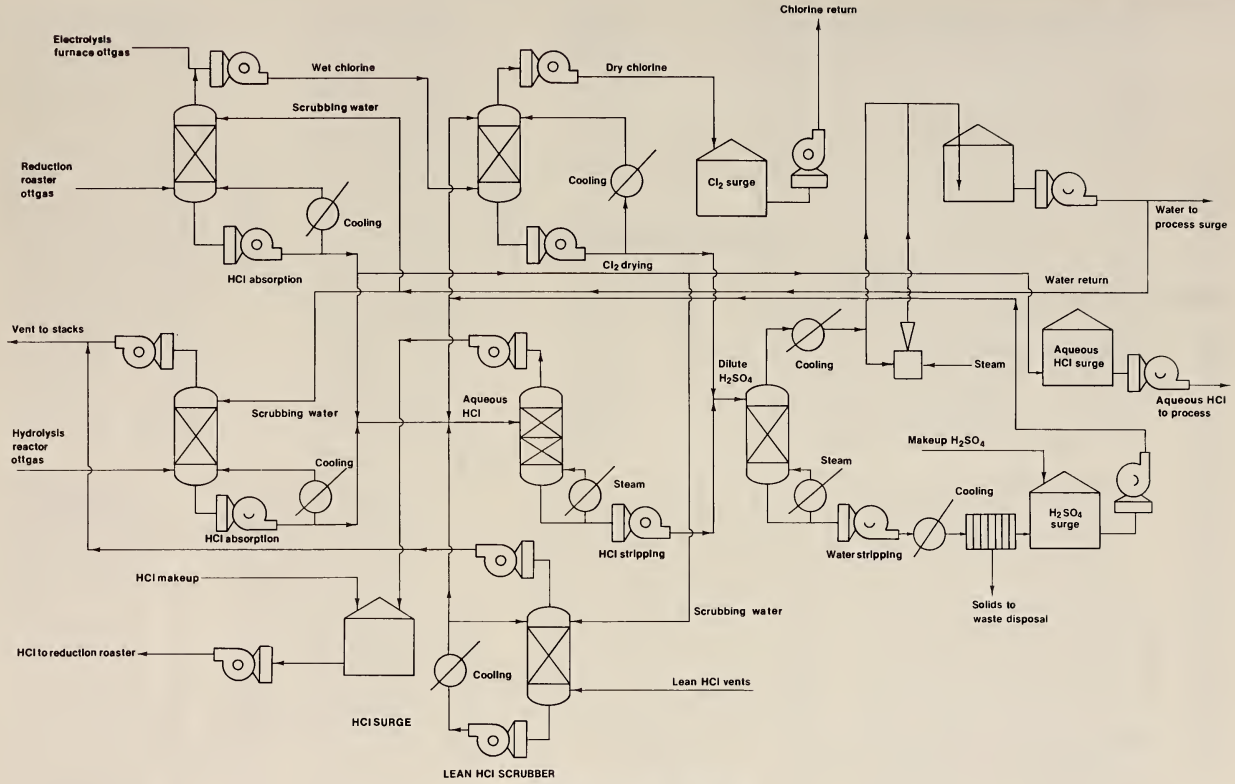


Figure D-12.—HCl recovery.

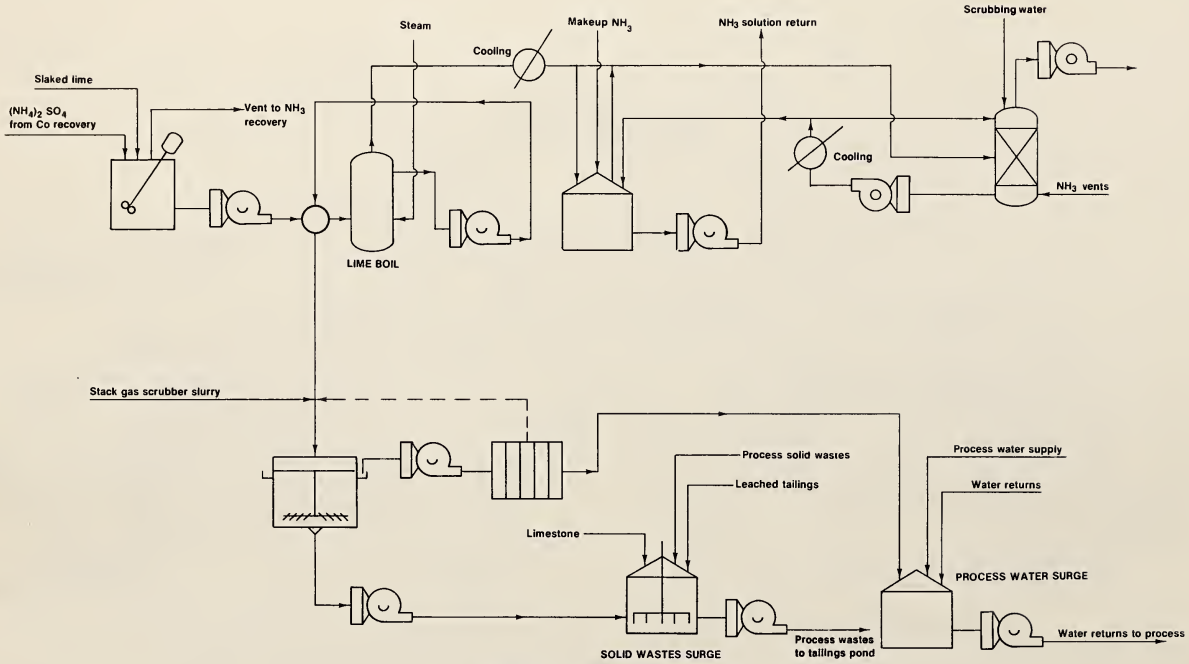


Figure D-13.—Waste recovery.

APPENDIX E.—SMELTING AND H_2SO_4 LEACH PROCESS

The smelting and H_2SO_4 leach process is a combination pyrometallurgical and hydrometallurgical treatment of nodules to recover the value metals Ni, Cu, and Co, with the option of recovering ferromanganese or a storable byproduct of Mn and Fe. The smelting process produces a slag, from which ferromanganese is recovered, and a metal alloy matte composed primarily of Ni, Cu, Co, and S.

The matte is granulated, slurried, and selectively leached with H_2SO_4 at elevated temperature and pressure. The leach residue and metalliferous solution are separated by a series of filtering and washing stages. After liquid-solid separation, copper and nickel are selectively extracted by liquid ion exchange (LIX) reagents, stripped from the ion exchange liquid into a weak electrolyte, and recovered as electrowon cathodes. Cobalt is separated from the raffinate by precipitation with hydrogen sulfide and recovered from the sulfide precipitate, along with some Ni, Cu, and Zn, by selective leaching and hydrogen reduction. Ammonia consumed in the process is recovered by lime boil and recycled to the process for use in pH control.

Detailed descriptions of each segment of the process are given for the following flowsheets. A summary of operating parameters for each section is given in table E-1. A key to the flowsheet symbols is given in figure E-1.

ORE PREPARATION AND DRYING (FIG. E-2)

Wet nodules are reclaimed from storage and fed through a primary cage mill, where they are reduced to minus ⅞ in. They then pass to a feed bin for delivery by a feed belt supplying nodules to a direct heated, fluid-bed drier for water removal.

REDUCTION (FIG. E-3)

The dried nodules are combined with coke, and the mixture is fed to a fluid-bed roaster for reduction with producer gas. After the roaster reduction, cyclones remove and return large particulates, while fine dust and hot gases pass to waste heat recovery and electrostatic precipitation. The reduced dust is delivered back to the process to recombine with the reduced products of the roaster. The reduction products are blanketed by an inert gas (such as nitrogen) and delivered by hoppers to the smelting furnace.

SMELTING (FIG. E-4)

Reduced nodules, comprised of MnO, FeO, a small amount of metallic Fe, the value metals Ni, Cu, and Co, and the less volatile components of nodules, are smelted with silica flux at about 1,425° C. An electric furnace of conventional design would be used.

Recoveries of Fe, Ni, Cu, and Co are in the range of 70 to 95 pct along with minor amounts of Mn. The iron alloy is subsequently removed and recycled to the smelting furnace as a molten silicate. The slag is comprised mainly of Mn, Fe, and SiO_2-Ca in the proper ratio for good slag fluidity and for subsequent production of ferromanganese.

CONVERTING (FIG. E-5)

Manganese reduction in the alloy is held at a level not exceeding 2.0 pct because it must be removed to less than 0.1 pct prior to reacting the Ni, Cu, and Co with S. Removal of the manganese and some iron is accomplished by addition of quartzite in the proper ratio to produce an eutectic mixture of the low-melting silicates. Oxidation of iron and manganese with 95 pct O_2 conserves heat for subsequent processing.

After the Fe-Mn-SiO_2 slag is removed as a first step, a near stoichiometric amount of S must be reacted to form Ni_3S_2, Cu_2S, and Co_9S_8. These sulfides are stable with respect to Fe and FeO at 1,200° to 1,400° C. The objective is to remove as much iron as possible without a major loss of the value metals to the exhaust gas or slag. Gypsum, reduced with coke, supplies the sulfur, and a fuel oil-oxygen burner supplies the heat for the reaction.

A top-blown rotary converter (TBRC) was selected for converter operations to provide intimate slag-metal-gas contact. All of the converting could be done in the same vessel, but two are shown in the flowsheet to assist visualization of the four-step process.

The third step is to add silica flux and blow the matte-iron alloy with air until the proper amount of iron is removed to balance its requirements in the ferromanganese alloy that is produced in another section of the plant. Alternatively, if iron in the nodules were low enough in relation to manganese, all of the iron silicate slag could be recycled to smelting.

As a final converting step, iron is lowered to 5 pct by a series of alternate blowing-slag removal-fluxing-blowing operations. The reaction is highly exothermic, requiring some care in prevention of Fe_3O_4 production.

The finished matte contains about 90 pct of the Ni, Cu, and Co and is removed by ladle to granulation.

FERROMANGANESE REDUCTION (FIG. E-6)

Ferromanganese can be produced from the smelter slag in an open air electric furnace with a reductant. Coke or several other carbonaceous materials would be suitable as reductants.

The reduction reaction requires intensive energy input from the electric arc. Because the charge is primarily molten, the bath surface will be exposed in molten form. Standard ferromanganese production is from cold ore, and a crust is present on the bath surface.

Medium carbon ferromanganese is produced, and a slag containing about 8 pct manganese is discarded as the final waste product from the hot metal operations.

MATTE LEACHING (FIG. E-7)

The molten alloy from converting is quenched in a granulation unit. The granulated alloy is rake classified, with oversize granules going to wet milling for final size reduction while classifier fines overflow to a clarifier, where they are settler thickened. The clarifier underflow recombines with wet mill effluent in a surge tank, while overflow returns to granulation. The matte slurry is pumped to an autoclave leaching vessel operated at 150 psig and 110° C. The leach products, dis-

Table E-1.—Operating parameters for smelting and H_2SO_4 leach process

Parameter and unit	Value
ORE PREPARATION AND DRYING (FIG. E-2)	
Feed rate, wet basis (330 days/yr; 24 hr/day ..... tpd..	10,900
Feed size ..... in..	-7/8
Drying temperature ..... ° C..	150
REDUCTION (FIG. E-3)	
Reduction gas:	
Producer gas ..... pct CO..	≈20
Other reductant ..... pct coke..	≈4.5
Reduction reactions:	
$MnO_2 + CO \rightarrow MnO + CO_2$	
$Fe_2O_3 + CO \rightarrow 2\ FeO + CO_2$	
$CuO + CO \rightarrow Cu + CO_2$	
$NiO + CO \rightarrow Ni + CO_2$	
$CoO + CO \rightarrow Co + CO_2$	
$Mo_2O_3 + 3CO \rightarrow 2Mo + 3CO_2$	
Metals reduction, pct:	
Co	90
Cu	90
Fe	100
Mn	100
Mo	20
Ni	90
Temperature, ° C:	
Solids	725
Gas	925
SMELTING (FIG. E-4)	
Temperature ..... ° C..	≈1,325
Retention time ..... hr..	2
Flux	Silica
Reductant	Coke, electrodes
Alloy recovery, pct:	
Co	90
Cu	90
Fe	70
Mn	2
Mo	85
Ni	95
Slag recovery, pct:	
Co	<10
Cu	<10
Fe	20
Mn	98
Mo	15
Ni	<10
CONVERTING (FIG. E-5)	
Slagging:	
Flux	Silica
Oxidant	O_2-air
Removal, pct:	
Fe	12
Mn	93
Final Mn ..... pct..	0.1
Converting and blowing:	
Flux	Silica
Fe removal ..... pct..	83
Final alloy (matte):	
Recovery, pct:	
Co	90
Cu	90
Fe	5
Mn	<.1
Ni	90
Slag discharge temperature ..... ° C..	1,400
FERROMANGANESE REDUCTION (FIG. E-6)	
Furnace type	Electric arc
Reductants	Coke, producer gas, electrodes
Alloy composition, pct:	
C	7
Fe	14
Mn	78
Si	1

Parameter and unit	Value
FERROMANGANESE REDUCTION (FIG. E-6)—Con.	
Slag composition, pct:	
SiO_2	47
Al_2O_3	15
CaO	22
MnO	8
Na_2O	4
MgO	3
MATTE LEACHING (FIG. E-7)	
Matte temperature ..... ° C..	1,325
Granulation temperature, initial ..... ° C..	95
Grinding method	Ball mill
Output particle size ..... mesh..	-325
Pulp density ..... pct..	9.5
Leaching:	
Temperature ..... ° C..	110
Pressure ..... psig..	150
Time ..... hr..	2
Leachate	H_2SO_4
Recovery, pct:	
Co	99
Cu	99
Fe	99
Mn	80
Ni	99
Washing efficiency ..... pct..	98
Filtration stages	2
pH ADJUSTMENT (FIG. E-8)	
Agent	$CaCO_3$
H_2SO_4 in-out	5-0.5
Solids removal method	Clarifier
COPPER LIQUID ION EXCHANGE (FIG. E-9)	
Extraction:	
Extractant	[1]LIX 64N
Number of stages	3
Organic-aqueous ratio	6:1
Metals extraction, pct:	
Co	0
Cu	100
Ni	0
pH (controlled by NH_3)	2.5
Temperature ..... ° C..	40
Stripping:	
Strip solution composition, gpl:	
H_2SO_4	160
Cu	40
Number of stages	2
Organic-aqueous ratio	2:1
Stripping, pct:	
Co	0.2
Cu	87
Ni	.9
Zn	100
COPPER ELECTROWINNING—COMMERCIAL (FIG. E-11)	
Current density ..... A/m^2..	180
Current efficiency ..... pct..	94
Temperature ..... ° C..	50
Cu in-out ..... gpl..	53-40
H_2SO_4 in-out ..... gpl..	160-180
COPPER RAFFINATE NEUTRALIZATION (FIG. E-12)	
Agent	NH_3 with air
Final pH	4
Solid removal method	Filtration with filter aid
NICKEL LIQUID ION EXCHANGE-EXTRACTION (FIG. E-13)	
Extraction:	
Extractant	[1]LIX 64N
Number of stages	3
Organic-aqueous ratio	7:1

[1]Reference to specific trade names does not imply endorsement by the Bureau of Mines.

Table E-1.—Operating parameters for smelting and H_2SO_4 leach process—Continued

Parameter and unit	Value
NICKEL LIQUID ION EXCHANGE-EXTRACTION (FIG. E-13)—Con.	
Extraction—Con.	
Co	1
Cu	1
Ni	99.5
Temperature, °C	40
Ammonia wash (primary):	
Washing agent, pct NH_3	1
Number of stages	2
Organic-aqueous ratio	3:1
NICKEL LIQUID ION EXCHANGE-STRIPPING (FIG. E-14)	
Ammonia wash (secondary):	
Scrub solution, gpl:	
H_2SO_4	1
$(NH_4)_2SO_4$	200
Number of stages	2
Organic-aqueous ratio	1:1
Stripping:	
Number of stages	3
Organic-aqueous ratio	6:1
Stripping, pct:	
Co	0.3
Cu	<.004
Ni	98.8
NICKEL ELECTROWINNING—COMMERCIAL (FIG. E-15)	
Current density, A/m^2	180
Current efficiency, pct	93
Temperature, °C	60
Ni in-out, gpl	75-50
H_2SO_4 in-out, gpl	0.016-40
Na_2SO_4, gpl	100
H_3BO_3, gpl	15
COBALT RECOVERY (FIG. E-16)	
Precipitating agent, pct NH_4HS	30

Parameter and unit	Value
COBALT RECOVERY (FIG. E-16)—Con.	
Metals precipitated, pct:	
Co	98
Cu	99.9
Ni	99
Zn	99.9
Temperature, °C	80
Clarifier underflow:	
Density, pct solids	5
Wash ratio	2:1
Leaching:	
Slurry density, pct solids	40
Agent, pct H_2SO_4	70
Evaporation-crystallization water removal, pct	70
Co oxidation:	
Temperature, °C	100
Pressure, psig	150
Co reduction:	
Temperature, °C	175
Pressure, psig	500
Reductant	H_2
AMMONIA RECOVERY (FIG. E-17)	
NH_3 recovery, pct	99
Temperature, °C	110
Underflow density, pct solids	60
NH_3 stripping:	
Pressure, atm	1.5
Recovery, pct	99
Number of stages	2
Direct condensation:	
Temperature, °C	40
Pressure, atm	1.3
Number of stages	1
NH_3 absorber:	
Temperature, °C	35
Pressure, atm	1.2
Number of stages	1

solved value metals and residue, are combined with other precipitated solids and fed to a two-stage countercurrent rotary drum filter-repulp operation. The filtered solids are pumped to waste treatment while the filtrate, which is now process pregnant liquor, is pumped to a pH adjustment circuit prior to selective metal removal.

pH ADJUSTMENT (FIG. E-8)

The pH adjustment process removes the necessary residual acid concentration of the pregnant liquor through the use of calcium carbonate (limestone). The precipitate (calcium sulfate) is removed by a clarifier, filtered, and the overflow is pumped to the copper LIX circuit.

COPPER LIQUID ION EXCHANGE (FIG. E-9)

The filtered pregnant liquor from pH adjustment passes to a three-stage countercurrent LIX circuit with interstage pH adjustment. Nearly complete transfer of Cu metal to the organic exchange liquid is accomplished along with trace exchanges of the Ni, Co, and Zn. The separated and loaded organic stream is countercurrently stripped of its copper value with depleted electrolyte from copper electrowinning. The copper electrolyte is heated on passage to electrowinning and cooled on passage from electrowinning to permit operation of electrowinning at a higher temperature. Makeup organic is added to the electrolyte-stripped reagent to offset degradation and soluble organic losses to pregnant liquor. A continuous purge to and recycle from a trace metal stripping step is operated to prevent a buildup of impurities (fig. E-10). The aqueous raffinate stream containing the nickel, cobalt, and trace metal values is sent to a neutralizing step prior to nickel recovery.

COPPER ELECTROWINNING—COMMERCIAL (FIG. E-11)

Cathode copper is recovered from the LIX strong electrolyte using conventional technology. Starter sheets of copper are deposited on titanium blanks, and are removed, washed, looped, and returned to the commercial section. Full-term cathodes produced in the commercial section are washed, unloaded, and prepared for shipment to sale. The major portion of the weak electrolyte is recycled to the LIX section for stripping, while a small purge stream is recycled to the pH adjustment process to prevent buildup of undesirable co-stripped metals other than copper. Makeup acid, used to redissolve scrap copper for return to the commercial cells for deposition, replenishes the weak electrolyte (a strong acid solution) for return to copper stripping. Sufficient steam, wash water, and makeup

water are added to the circuit to offset water vaporized and carried off with evolved oxygen during electrowinning.

COPPER RAFFINATE NEUTRALIZATION (FIG. 12)

The Ni-bearing solution from the Cu ion exchange process contains an excess of acid, which must be neutralized and made slightly basic with ammonia and oxidized before the Ni values can be removed without coextraction of Co. In addition to neutralization, tank aeration causes precipitation of the Fe, Mn, Mg, and Al initially extracted from the matte and carried with the raffinate.

The collected precipitated solids are sent to disposal. The pH adjusted filtrate containing some entrained precipitate passes on to nickel LIX.

NICKEL LIQUID ION EXCHANGE-EXTRACTION (FIG. E-13)

The neutralized raffinate is filtered of entrained precipitate, then nickel is separated in three stages of pH-controlled countercurrent extraction with an organic ion exchange extractant. Other trace metals and ammonia are exchanged along with the nickel. The nickel-stripped raffinate containing primarily cobalt is sent to cobalt separation. Entrained aqueous solution and dissolved ammonia are removed from the organic phase. The entrained aqueous solution is removed in a physical liquid-liquid separation step. The ammonia is partially removed in a two-stage countercurrent aqueous wash of organic followed by steam stripping of the ammonia. The organic phase is then sent to nickel stripping.

NICKEL LIQUID ION EXCHANGE-STRIPPING (FIG. E-14)

The partially ammonia-stripped organic passes to a second stage for reaction with sulfuric acid to draw the remaining ammonia into an aqueous phase. The phases are countercurrently contacted and separated in two stages. The aqueous phase returns to nickel extraction. The organic phase, containing nickel and trace metal impurities, enters two countercurrent stages of nickel stripping with weak electrolyte from electrowinning. This electrolyte is heated-cooled in going to-from the electrowinning operation, which is operated at a slightly higher temperature than stripping. The nickel-free organic is replenished of losses with fresh organic. A small amount of organic is purged to a trace metals removal step to prevent impurity buildup. The "cleaned" organic purge and makeup organic are combined with the nickel-free organic for recycle to the nickel ion exchange extraction step.

NICKEL ELECTROWINNING—COMMERCIAL (FIG. E-15)

Nickel is recovered from the strong electrolyte by electrowinning in a manner similar to that used for copper recovery. In the nickel electrowinning, however, cathode bags are used, and the strong electrolyte is chemically conditioned with sodium sulfate and boric acid to control conductivity and pH. Dissolved organic, carried from the LIX step, is adsorbed in an activated carbon bed prior to any electrolyte passing to electrowinning. The bed is periodically isolated from the system and steam stripped of organic. Nickel is recovered in a manner similar to that used for copper recovery. The starter sheets are pickled in H_2SO_4 prior to use in the commercial cells, and nickel scrap is redissolved in ammonia-containing raffinate and recycled to the ion exchange process. The electrolyte purge required to remove impurities from the electrowinning circuit passes to raffinate neutralization. The strongly acidic, depleted electrolyte returns to the nickel stripping circuit.

COBALT RECOVERY (FIG. E-16)

Along with unextracted Cu, Ni, and Zn, Co is recovered from the Ni LIX raffinate by precipitation with ammonium hydrosulfide (produced by sparging hydrogen sulfide into an excess of ammonia solution). The sulfide precipitate is separated from the raffinate in a clarifier. The clarifier overflow is filtered of entrained precipitate and sent to ammonia recovery. The underflow is mixed with electrolyte purges from Cu and Ni electrowinning as well as the Co recovered from stripping of the LIX reagent. The mixture is pressure leached with air to preferentially dissolve the Ni and Co sulfides, leaving Cu and Zn sulfides in the residue. The latter are removed by filtration and sold as minor products to smelters for recovery of metal values.

Following pH adjustment and reprecipitation with hydrogen sulfide for final removal of any Zn and Cu solubilized in the first leach, the Ni-Co sulfate solution is heated and autoclaved, and Ni reduced with hydrogen. Sufficient ammonia solution is added during reduction to neutralize the acid formed. Only a portion of the nickel is removed per pass to prevent overreduction and subsequent contamination of the nickel powder with cobalt. After densification through repeated recycle, the nickel powder is removed, washed, and passed to drying and briquetting for sale.

The largely nickel-free cobalt sulfate solution passes to an evaporator-crystallizer where the remaining nickel and cobalt are precipitated as the double salts with ammonium sulfate. Excess ammonium sulfate is purged, and the salts are redissolved in a strong ammonia solution. The cobalt is oxidized to the cobaltic state (Co^{3+}) with air to enable cobalt to remain in solution. The stream is subsequently acidified to remove the nickel salts that are separated and recycled to the pH adjustment step. The nickel-free solution is then heated and autoclaved for removal of cobalt by hydrogen reduction. Sufficient ammonia is added to neutralize the acid generated. The cobalt powder is dried and briquetted for sale, and the ammonium sulfate is purged to ammonia recovery.

AMMONIA RECOVERY (FIG. E-17)

The raffinate from cobalt recovery, containing process ammonium sulfate and ammonia, is countercurrently contacted with slaked lime in a steam strip or boil step to recover the ammonia value of the sulfate. The gypsum precipitate from the lime boil enters a settler, then underflows to the waste surge tank for disposal. The overflow liquor is recycled to the granulation-leach-washing circuit. Steam sparged into the lime boil strips ammonia, which then passes to a three-stage ammonia condenser-absorber circuit. The aqueous absorbed ammonia solution returns to the process at required locations. The ammonia-containing vent gases of the process are passed through ammonia recovery. Scrubbed vent gas is discharged to the stack for disposal.

WASTE TREATMENT

Molten waste slag from ferromanganese production and

converting is granulated by spraying it with large quantities of process waste water and makeup water, with heat removed by evaporation. Gases from smelting and converting pass through electrostatic precipitators for dust removal. Reducing and sulfur-containing gases are directed to the main boilers for combustion and subsequent cleaning; clean gases are scrubbed directly. Process dusts are conditioned by wetting and agglomerating with lime. Sulfurous dusts are recycled to the sulfidizing converter, while other dusts are returned to smelting and/or purged, as required, to control the buildup of heavy metals in the ferromanganese product. All process solid and liquid effluents are collected, neutralized, and pumped to the waste disposal area.

PLANT SERVICES

Plant services include process and cooling water supply and treatment, steam raising and power generation, stack gas treatment, and producer and dryer gas production. Makeup water is clarified and softened for distribution to the process, as required. Additional treatment is required for cooling tower water makeup, boiler feed water makeup, and supplying plant potable water. Offgas hydrogen from cobalt recovery and offgases from reduction and smelting steps are burned in the main boiler, along with coal, to raise the required process steam and generate a portion of the power required in the process. Following particulate removal, the flue gases are combined with other process offgases and pass to gas treatment, where sulfur oxides and other acidic constitutents are removed by scrubbing with limestone. The scrubbed offgases are reheated, combined with scrubbed vents from various process steps, and passed to stacks for disposal.

Gas for nodules reduction is produced in a two-stage entrained flow gasifier in which coal is mixed with preheated air and high-temperature steam for the production of a carbon monoxide-rich reducing gas. The gasifier product passes directly to reduction following particulate removal and energy recovery, with sulfur removal from this and other boiler flue gases taking place after combustion. Coal is also used in production of hot combustion gas for nodule drying.

PROCESS ALTERNATIVES

The processing scheme proposed for the recovery of metal values from nodules has been based on a very limited amount of published data on nodule properties and behavior under smelting-converting conditions. The matte processing (hydrometallurgical) operations would be essentially the same as those used in direct high-temperature acid leaching of the nodules.

At the present time, the only known production of matte from lateritic nickel ore is carried out directly in low-shaft blast furnaces, followed by converting. Societe Métallurgique le Nickel employs a blast furnace on New Caledonian laterites. The conventional process requires gypsum and coke in the burden to supply the sulfur, while sodium sulfate is used for this purpose in Japan. A preliminary step of nodule smelting to an alloy is necessary, because manganese oxide preferentially reacts with sulfur. Electric furnace smelting of laterites is widely practiced, but the product is ferronickel instead of matte. Manganese nodules, however, contain too much copper and cobalt to yield a marketable ferroalloy product, and must be further upgraded by mechanical or hydrometallurgical methods.

The drying, reduction, and smelting steps could be more thermally efficient (independent of waste heat boiler considerations) if the hot reduction offgases were used for nodule drying. Circular grates, grate kilns, and other counter-current contactors have been designed to combine the drying-reduction step, but only the blast (shaft) furnace concept is known to combine the reduction with smelting. Fluid-bed dryers and reduction or calcination roasters are generally state-of-the-art choices.

Alternate types of converter designs should meet the objective of high Ni, Cu, and Co recovery from matte containing less than 5 pct Fe. Pierce-Smith (P-S) converters of various designs are more widely used than TBRC's, but the TBRC is a suitable replacement.

Pyrite is often used to sulfidize laterites and could be used to sulfidize nodule smelting alloy. A total of 95 tpd of pyrite would be required to replace 265 tpd of gypsum, if equal sulfur utilizations were possible, and energy requirements would be reduced. However, it is possible that sulfur utilization could be poorer, which would impose an added burden on the gas-cleaning system.

A possible option for recovery of metals from matte would be the HCl leaching process used by Falconbridge Nikkelverk AS in Norway. Nickel is preferentially dissolved with HCl, then iron and cobalt are solvent extracted. Nickel chloride is hydrolyzed after HCl is stripped, and nickel oxide is marketed. Copper is recovered from the matte residue by sulfation roasting and electrowinning. Cobalt recovery is similar to the process selected in this appendix.

Another possible method of matte upgrading is practiced by INCO. The process depends upon cooling a matte at a slow rate so that alloy phases separate from a sulfur matte. The alloy is then recovered by crushing and a magnetic separation-flotation cycle. Recovery by this method is of the order of 50 pct and requires recycle of the matte.

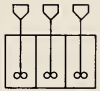
While a number of options was considered for recovering the metals from matte, the chosen route involves a H_2SO_4 leach with oxidation of the sulfides, followed by conventional LIX and electrowinning. This option has been implemented in essence by Outokumpu Oy and AMAX on copper-nickel matte from conventional ores.

The Cu raffinate neutralization step, which assumes the use of enough ammonia to generate a basic solution and oxidation of Co to prevent coextraction with Ni, could be eliminated if a reagent could be found to selectively remove Ni in the presence of Co. The precipitation-separation of basic salts of Fe, Mn, Mg, and Al would be eliminated with a saving of necessary equipment.

In the selected flow scheme, the ammonium sulfate solutions purged from the LIX extraction and the copper raffinate neutralization have been treated with lime for the recovery of ammonia for recycle. An alternative approach would involve direct recovery of ammonium sulfate by evaporation-crystallization for sale as a byproduct. The alternative is highly energy intensive because of the number of crystallizing-evaporating steps necessary to produce a relatively pure byproduct from a stream containing many entrained process impurities.

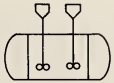
Alternative configurations of the metals separation steps are possible, such as selective extraction-selective stripping, but their impact on overall plant material and energy balances should be minor. Many variations are possible in the details of the scheme used for recovery of cobalt from a mixed sulfide precipitate. The impact on plant requirements would not differ appreciably from the present approach because the sulfides will still be oxidized to sulfates, purged, and hydrogen reduced. It does not appear likely that the solution could be purified easily enough to permit recovery of electrolytic cobalt.

Absorber



Aerator

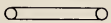
Agitator



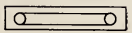
Autoclave

Blower

Centrifuge



Conveyor



Covered conveyor

Cyclone

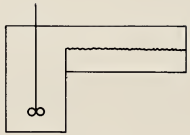
Ejector

Filter

Filter

Heat exchanger

Hopper

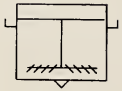


Mixer-settler

Pump

Surge tank

Surge tank, agitated



Thickener

Figure E-1.—Key to symbols.

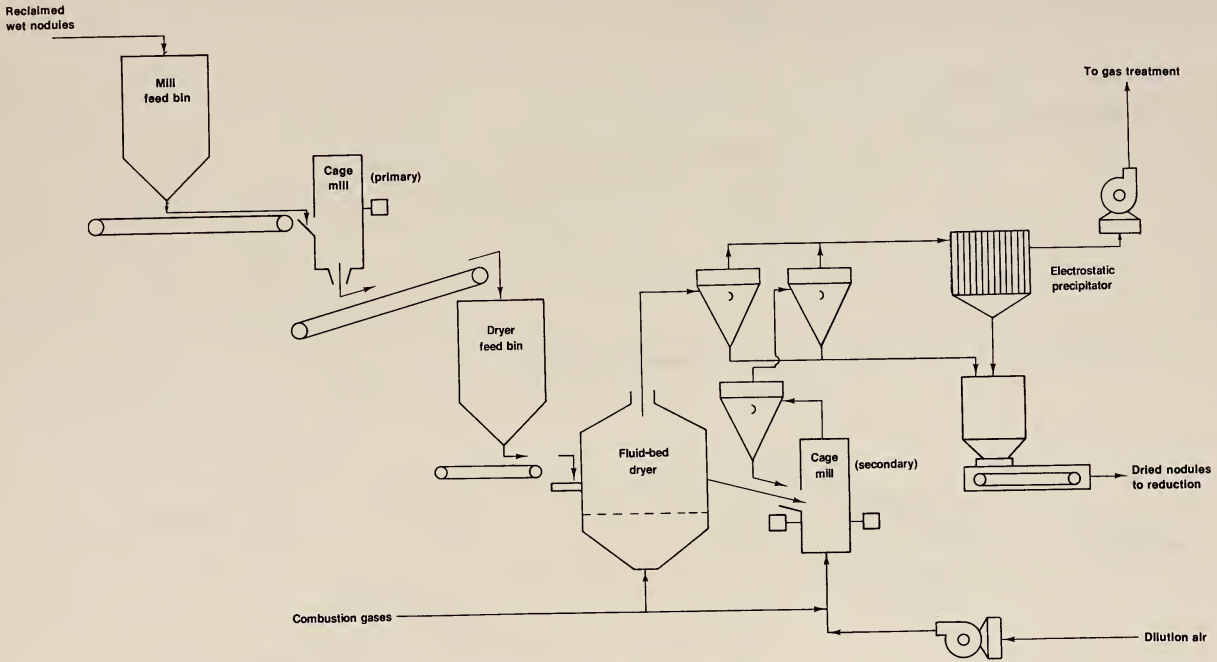


Figure E-2.—Ore preparation and drying.

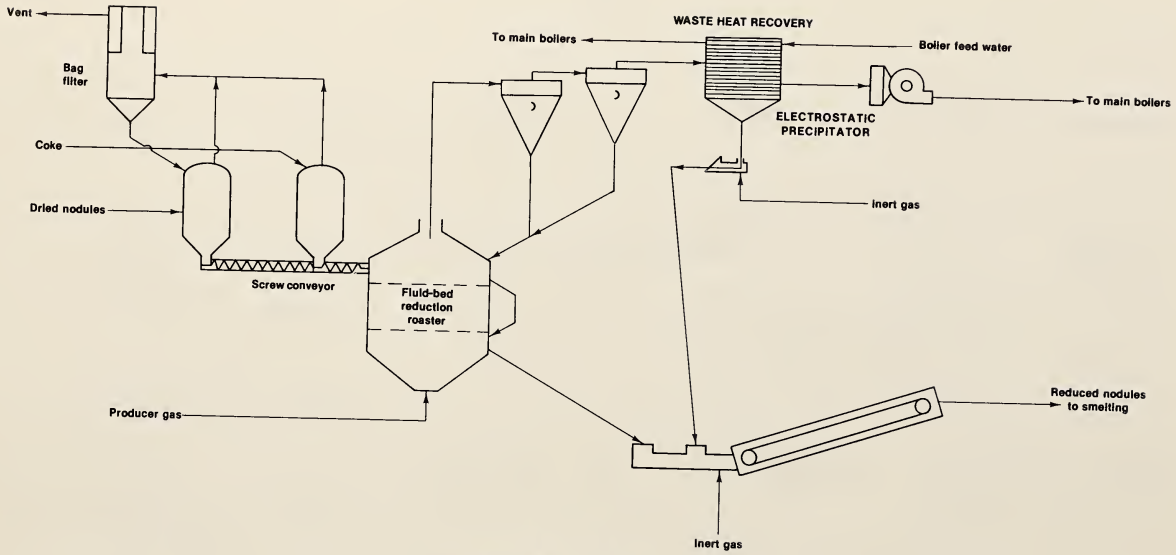


Figure E-3.—Reduction.

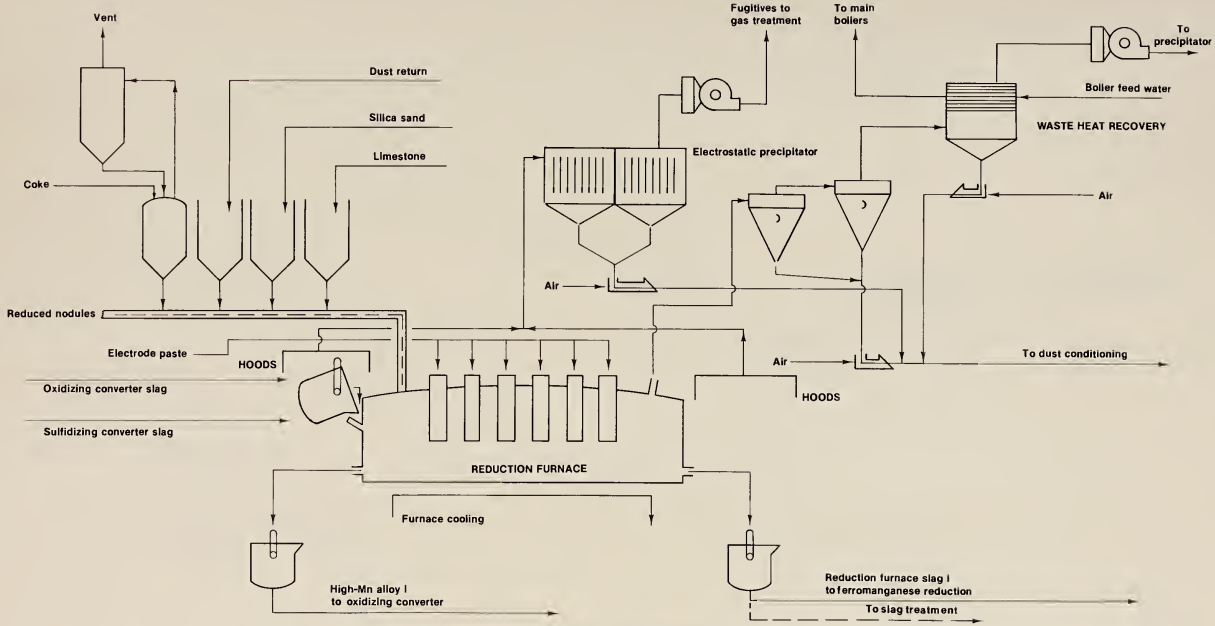


Figure E-4.—Smelting.

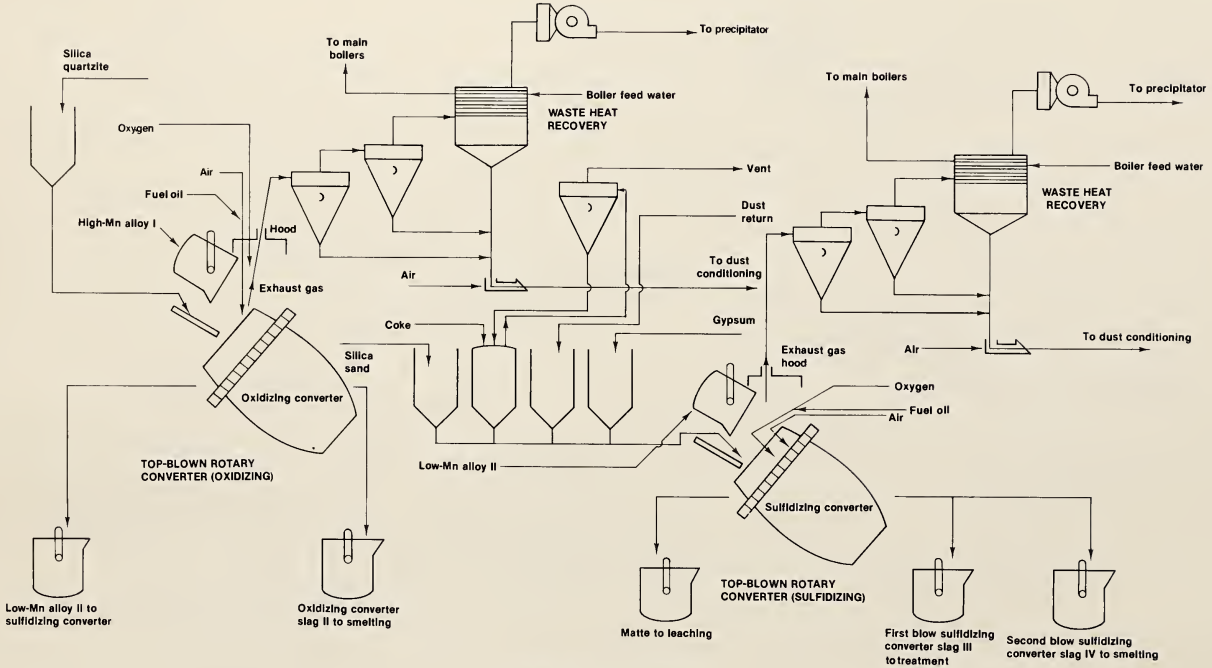


Figure E-5.—Converting.

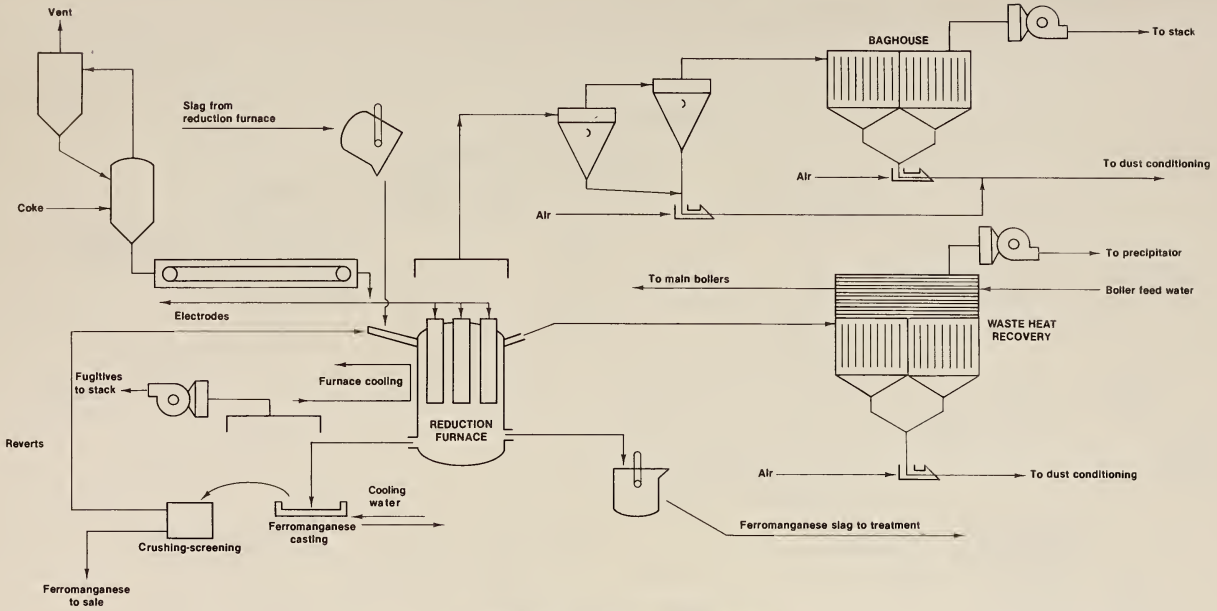


Figure E-6.—Ferromanganese reduction.

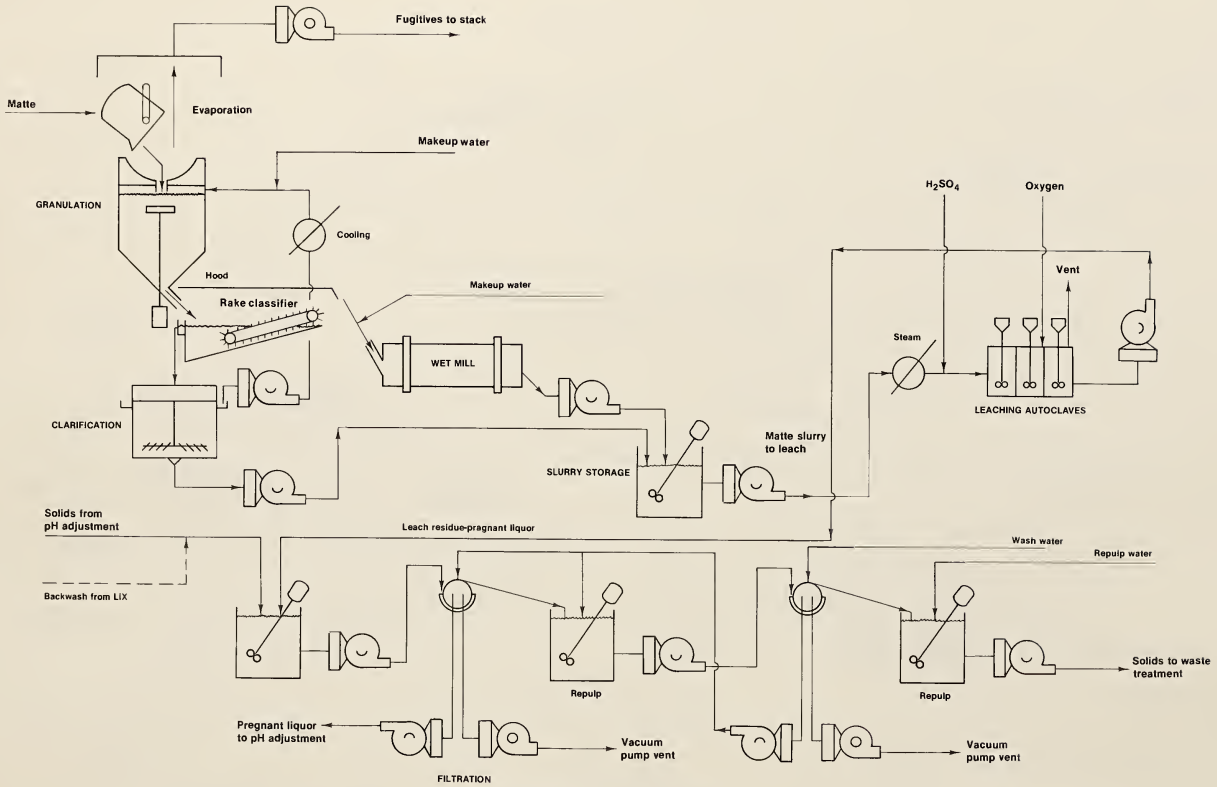


Figure E-7.—Matte leaching.

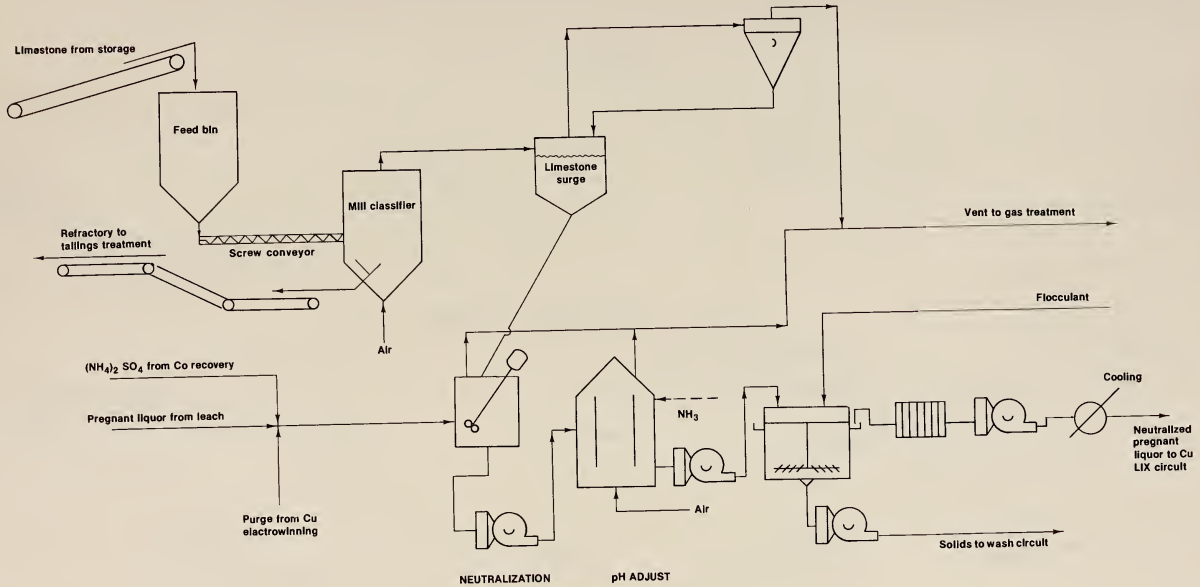


Figure E-8.—pH adjustment.

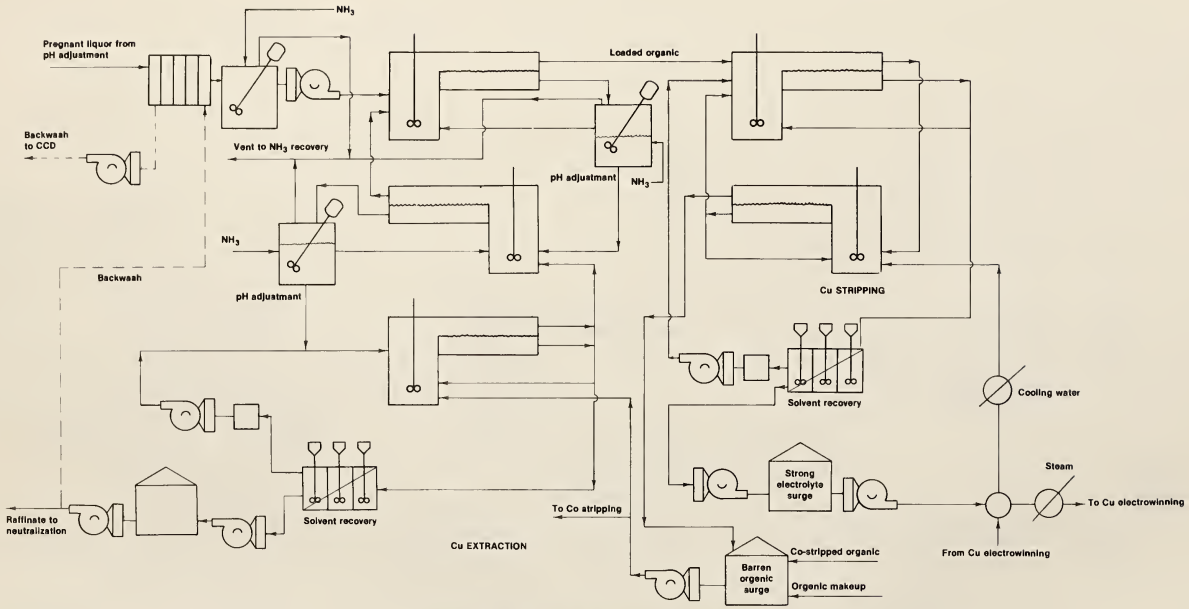


Figure E-9.—Copper liquid ion exchange.

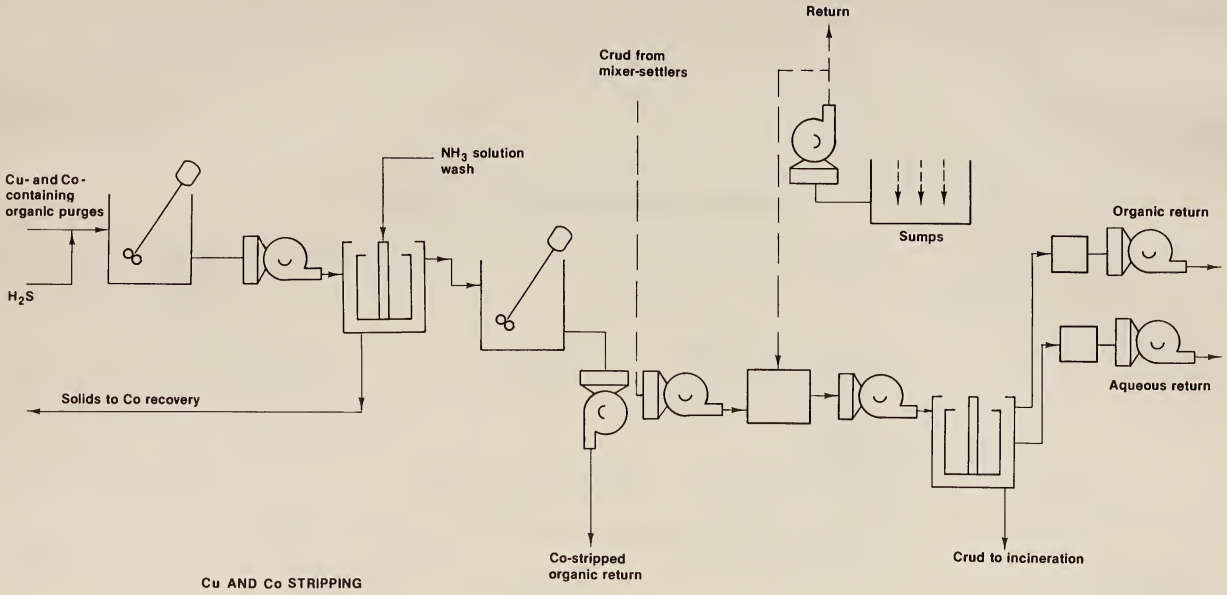


Figure E-10.—Cobalt stripping-organic purge.

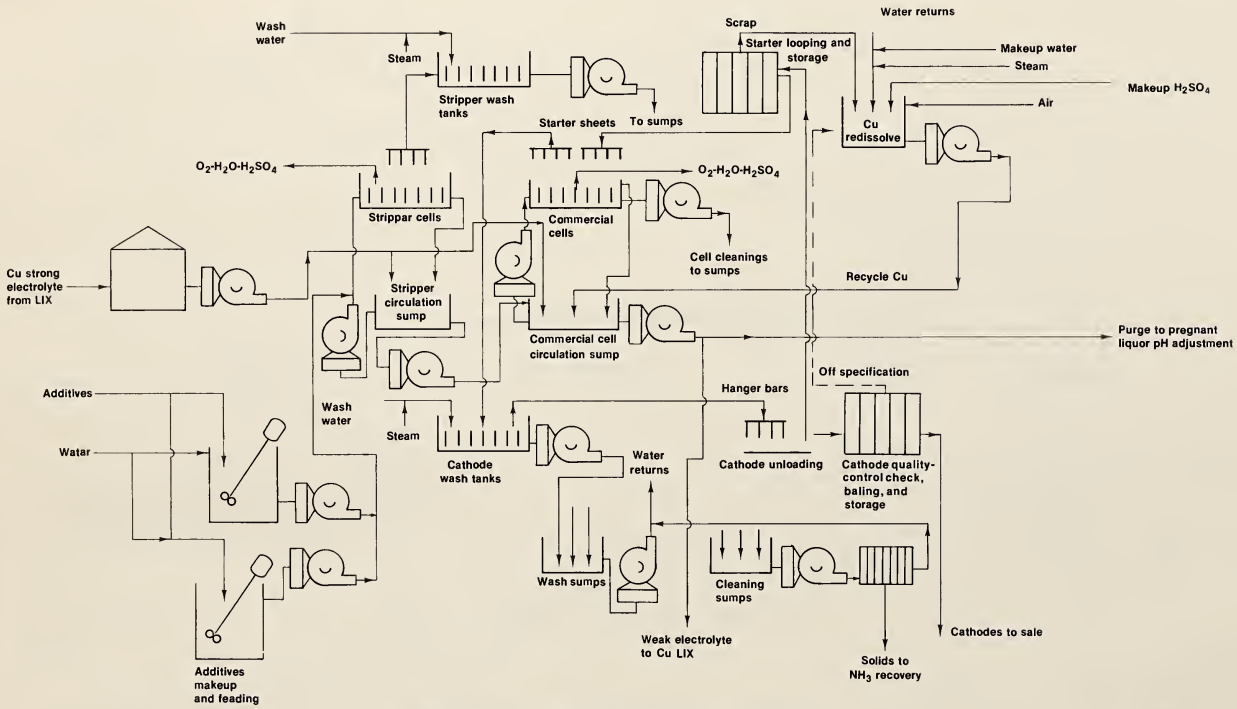


Figure E-11.—Copper electrowinning—commercial.

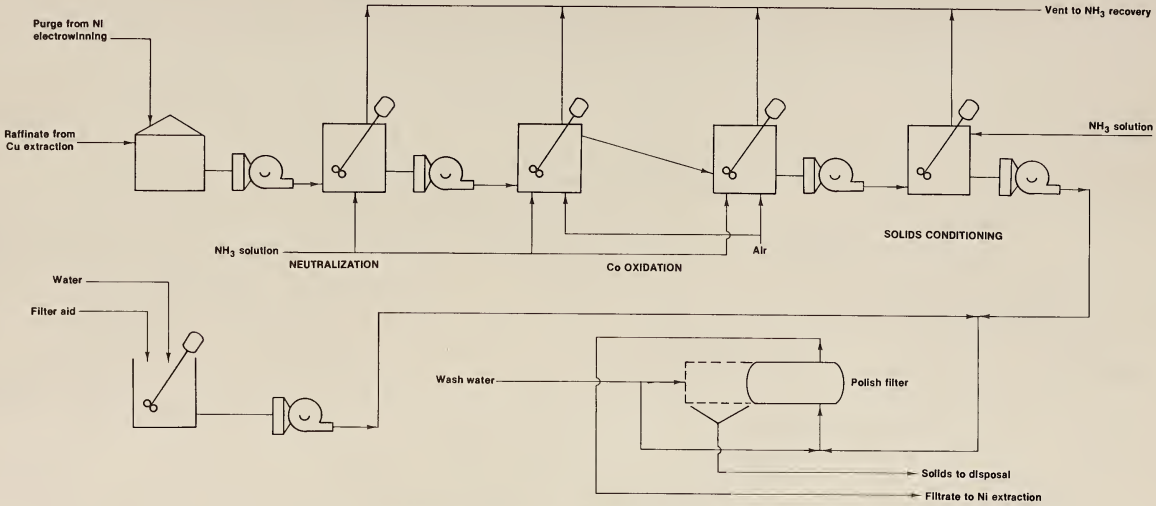


Figure E-12.—Copper raffinate neutralization.

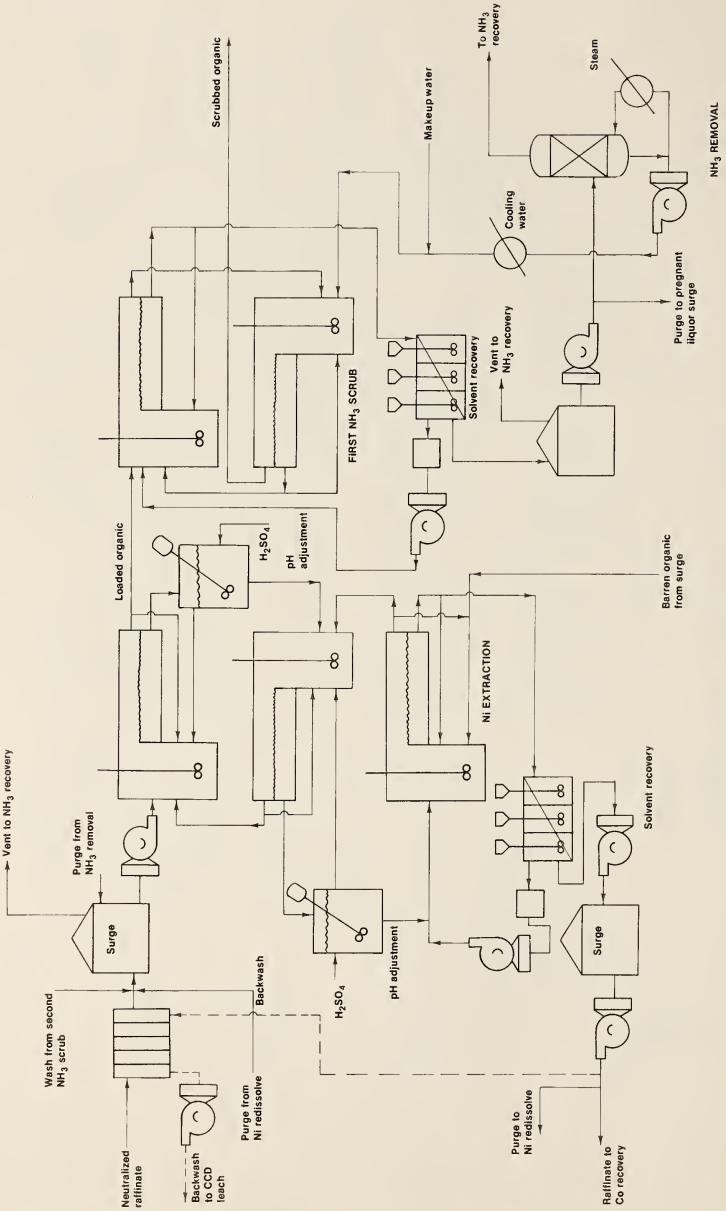


Figure E-13.—Nickel liquid ion exchange-extraction.

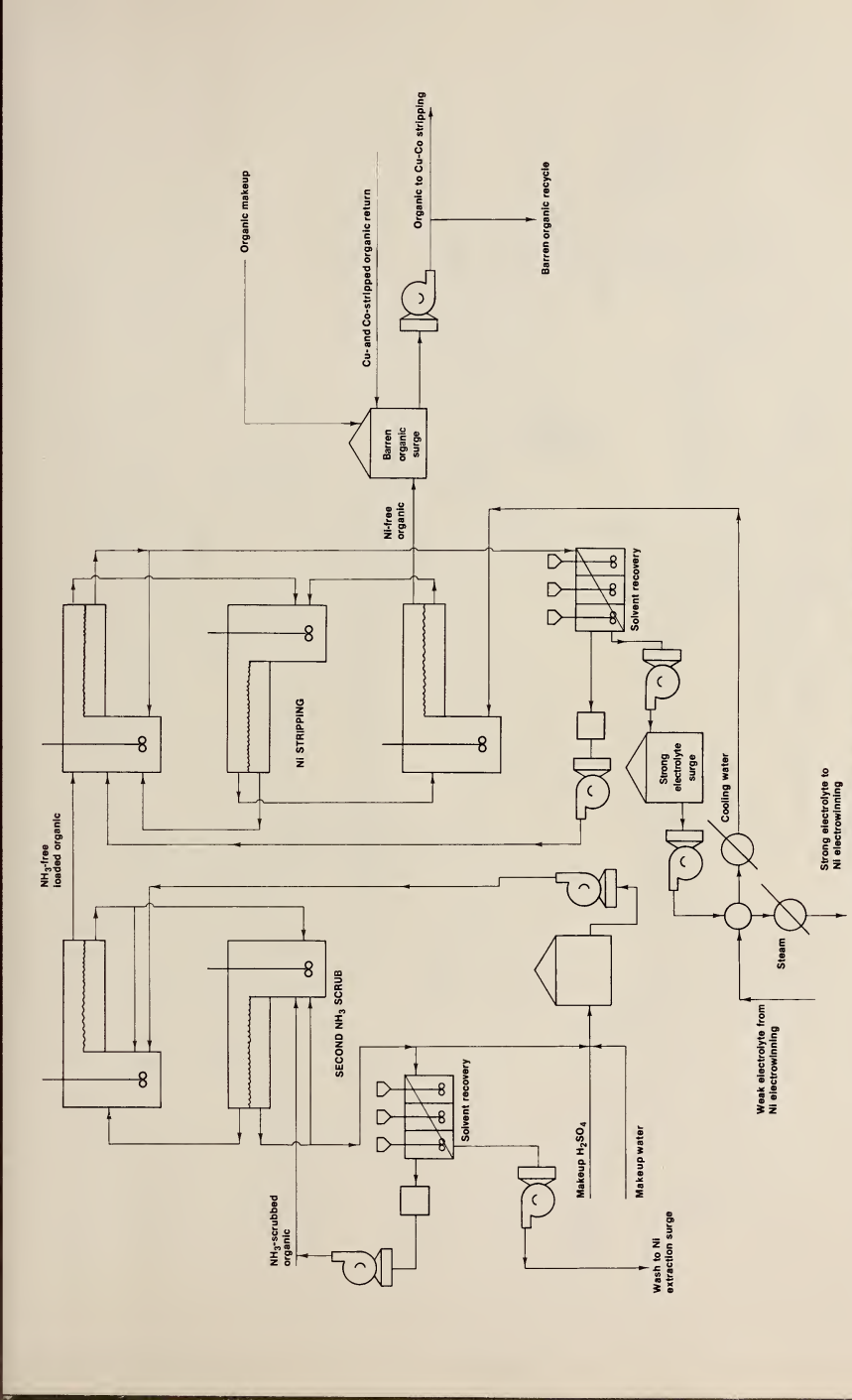


Figure E-14.—Nickel liquid ion exchange-stripping.

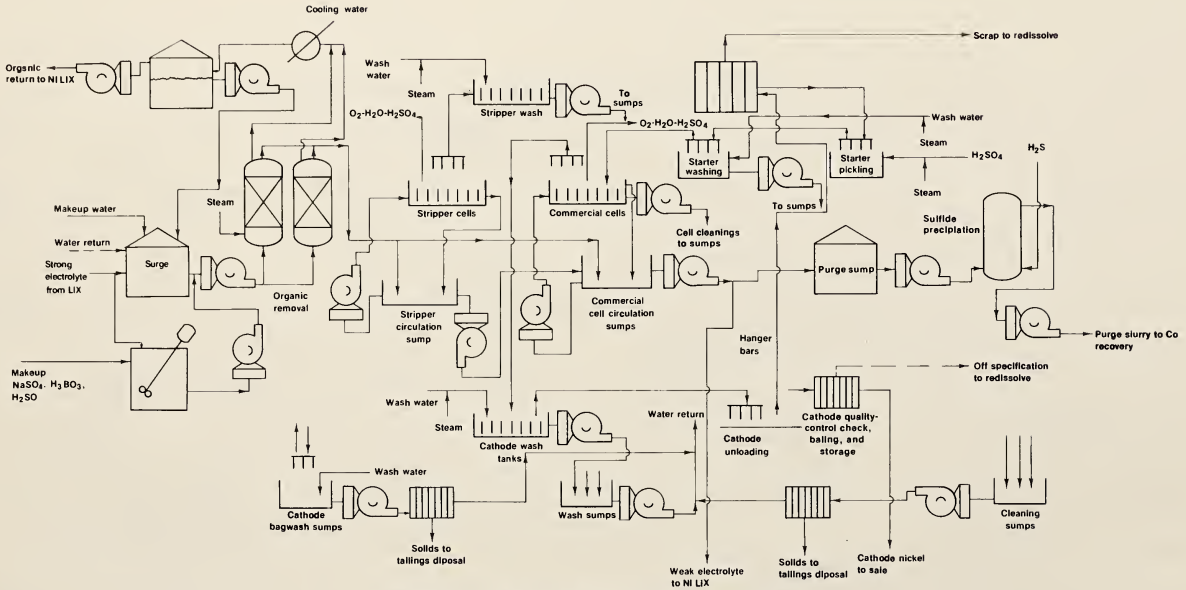


Figure E-15.—Nickel electrowinning—commercial.

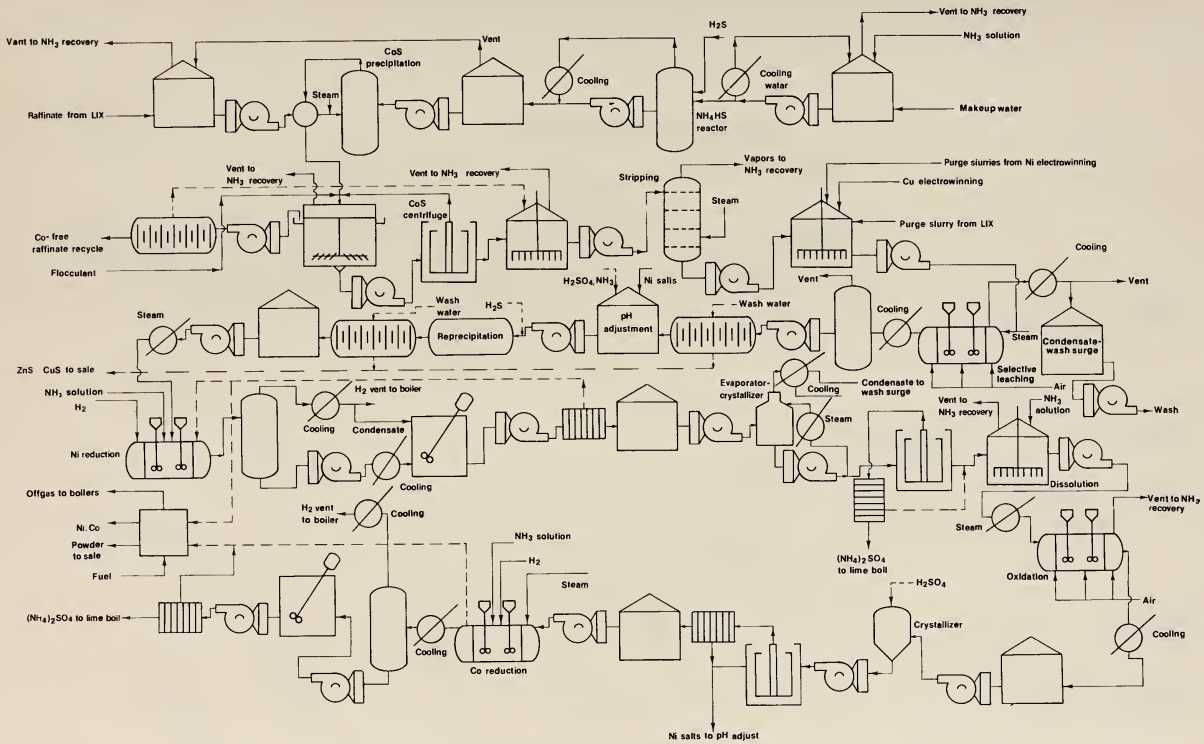


Figure E-16.—Cobalt recovery.

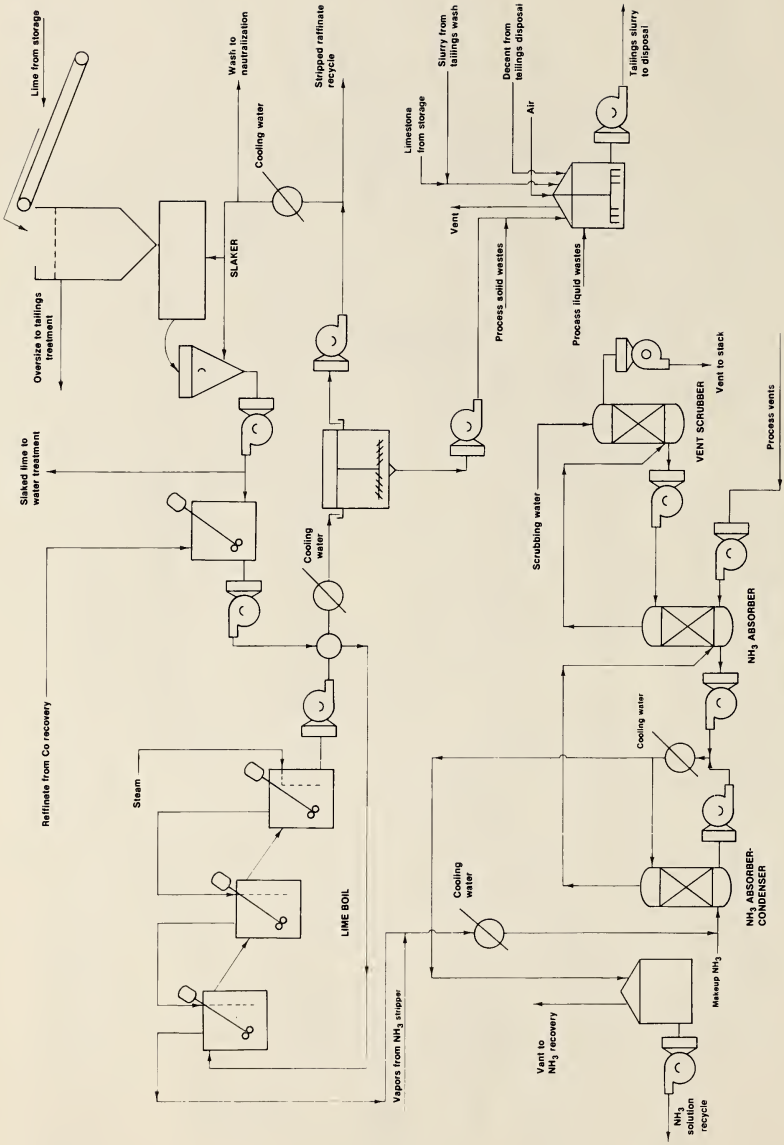


Figure E-17.—Ammonia recovery.

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